ADVANCES IN NANOCOMPOSITES - SYNTHESIS, CHARACTERIZATION AND INDUSTRIAL APPLICATIONS

Edited by Boreddy S. R. Reddy

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Advances in Nanocomposites - Synthesis, Characterization and Industrial Applications Edited by Boreddy S. R. Reddy

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Preface

Advances in Nanocomposites - Synthesis, Characterization and Industrial Applications was conceived as a comprehensive reference volume on various aspects of functional nanocomposites for engineering technologies. The term functional nanocomposites signifies a wide area of polymer/material science and engineering, involving the design, synthesis and study of nanocomposites of increasing structural sophistication and complexity useful for a wide range of chemical, physicochemical and biological/ biomedical processes. "Emerging technologies" are also broadly understood to include new technological developments, beginning at the forefront of conventional industrial practices and extending into anticipated and speculative industries of the future.

The book fills the gap between what you have learnt at the University and what you actually do practice in industry. It explains the major concepts of new advances in nanocomposites and their applications in a friendly, easy to understand manner and provides practical knowledge in different aspects of nanocomposites. This makes a transition from a college student to a "professional researcher" much easier.

The choice of materials for multi-author complications is always subject to a number of periodical and judicial limitations. These limitations notwithstanding, I have been privileged to benefit from the cooperation of many leading experts in nanocomposites, and also a number of senior researchers of well-known companies at the forefront and nanocomposites not frequently disclosed elsewhere. I must, in particular, acknowledge the courtesy of all the contributors in allowing me to organize their contributions in producing a cohesive and correlated compilation, and to minimize overlaps between closely related chapters.

The scope of the present book on nanocomposites and applications thus extends far beyond emerging technologies. This book presents 40 chapters organized in four parts systematically providing a wealth of new ideas in design, synthesis and study of sophisticated nanocomposite structures.

Part 1 introduces a wide selection of 14 chapters on synthesis of nanocomposites. The topics covered include core shell, quantum dots, thermal properties, structural, metal/ polymer nanomaterials, PET-MMT and PET-PEN-MMT nanocomposites, nanosized luminescent materials, nanocomposites – theory, properties and applications, hydroxy-apatite/collagen bone-like nanocomposites, poly(dimethylsiloxane-urethane) nano-composite membranes, rheology-morphology interrelationships for nanocomposites, nanocomposites, nanocomposites and electrode in proton exchange membrane

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fuel cell, characterization and application of nanocomposites, and sol-gel route to nanocomposites..

Part 2 comprises of 14 chapters devoted to electrochemical properties of oxide-matrix nanocomoposite materials, composite materials, devices for cancer thermochemotherapy, electrokinetic properties, conducting polymers for EMI, electrospinning fabrication, electrodeposition of metal matrix, effects of Cu addition on the microstructures, spark plasma sintered NdFeB, anticorrosive coatings, NdFeB nanocomposite thin films, fuel cell application and corrosion behaviour of Ni/Al₂O₃.

Part 3 relates to 8 chapters pertaining to carbon nanotubes about fabrication of micro composite components, nanowire-polymer nanocomposites, PBT containing carbon nanotubes, ion-induced carbon nanocomposite fibers, epoxy-carbon nanotubes reinforced composites, damping capacity of MWCNTs, nano reinforcements in surface coatings and thermal conductivity of PEEK/ZrO2 coated MWCNTs.

Part 4 discusses gas sensors dealing with films, mechanical alloying, nanocomposite metal oxides and steam reforming of methane.

I would like to place on record that one of my Senior Research Fellows, Mr. D. Gnanasekaran, helped me in my editorial work to bring out this book successfully.

BSR Reddy, Director Grade Scientist 'G' and Head, Industrial Chemistry Laboratory, Central Leather Research Institute, Adyar, Chennai-600 020, India

Part 1

Synthesis

Preparation and Characterization of Inorganic-Organic Nanocomposite Coatings

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1. Introduction

In recent years, more and more researchers are devoted themselves to studying nanocomposite hybrid materials. Since, the combination of different components in the nanosize range can yield new materials that may combine the advantages of each component and nanomaterials. Inorganic - organic hybrids nanocomposite materials is an example of this kind of materials, which have become a creative alternative with unusual features of the materials in industry. In fact, the art of combining dissimilar components to yield improved materials is not new. It goes way back to ancient construction materials like Adobe (Gomez-Romero et al., 2001). He used to build houses and buildings by a mixture made from the clay (inorganic) and straw (organic), where the straw was provided the mechanical properties for clay. However, the modern concept of hybrid materials goes way beyond the concept of a mixture between their components, actually falls between the concept of a mixture and a compound. A compound is formed by carrying out a chemical reaction between their components, where the properties of each part are eliminated to form a new material with different properties. In a mixture, a physical interaction between the components is involved. Whereas, the hybrid concept falls into a category where the interphase between their components is increased compared to a mixture, and their interactions will be at the molecular level (Judeinstein et al., 1996; Yacaman et al., 1996).

The main idea in development of the *hybrid materials was to take advantage of the best properties of each component that forms a hybrid, trying to decrease or eliminate their drawbacks getting in an ideal way a synergic effect; that results in the development of new materials with new properties.*

The first interest in the development of hybrid materials was mainly based on the design of hybrid polymers with special emphasis on structural hybrid materials. A variety of silicates, polysiloxanes etc. modified with organic groups or networks for improvement of mechanical properties, were the first type of hybrid materials investigated.

The expectations for hybrid materials go further than mechanical strength, such as thermal and chemical stability. Magnetic hybrids (tricarboxilic substituted radical and Cu ions), Electronic hybrids used in electronics (transistors, diodes), and Functional Hybrids. Considering that, the main characteristics of functional hybrid materials bind to the chemical activity of their components, exploring their optical and electrical properties, luminescence, ionic conductivity, and selectivity, as well as chemical or biochemical activity, give a way to the materials that can be applied for: sensors, selective membranes, all sorts of electrochemical devices, from actuators to batteries or electrochemical supercapacitors, supported catalysts or photoelectrochemical energy conversion cells, etc. So, highly sophisticated surface related properties, such as optical, magnetic, electronic, catalytic, mechanical, chemical and tribological properties can be obtained by advanced nanostructured coatings, making them attractive for industrial applications in high speed machining (Veprek, et al., 1995, 2001), tooling optical applications and magnetic storage devices because of their special mechanical, electronic, magnetic and optical properties due to size effect (Andrievski et al., 2001; Cantor et al., 2001); Mazaleyrat, et al., 2000; Provenzano et al., 1995).

Taking into account the great diversity of extended and molecular inorganic species, small organic molecules and available polymers for the design of the hybrid materials, it is clear that the variety of combinations is tremendously enormous. The wide range of possible hybrids would include innovative combinations, starting from inorganic clusters, fullerenes or metal nanoparticles dispersed in organic polymers to organic and organometallic molecules, biomolecules or enzymes dispersed in inorganic sol-gel polymers, or macrocycles or polyethylene oxide chains intercalated into silicate minerals.

In general, the inorganic-organic hybrid materials can be classified by using several criteria's based on their field of application or on their chemical nature. If we consider classification on the chemical bonding as a base, it would result more useful to distinguish common characteristics and would help us understanding related behaviors and properties. In this case, classification of inorganic-inorganic materials, based on the chemical bonding nature between organic-inorganic interphase will be consisted of two major groups: Class I, where organic and inorganic components are embedded and only weak bounds (ionic bonds, hydrogen bonds or Van der Waals interactions) give the cohesion to the whole structure; and in Class II, where two components are linked together through strong chemical bonds (covalent, iono-covalent or coordination bonds). In tis work we will consider a very simple and logic classification based on the morphological combinations of the inorganic –organic hybrid components as fellow (Bier, et al., 2002):

- Class 1. Inorganic matrix systems: where organic materials were embedded in an inorganic polymer. Synthesis of nanohydroxyapatite composite based on combining HA matrix and organic polymers, especially those showing the proper bioactivity, can be considered as an example of this category.
- Class 2. Organic matrix systems: where inorganic materials are embedded in an organic polymer. Some of the oldest and well-known organic-inorganic hybrids of this category are used in the paint industry by dispersion of the inorganic pigments into organic binders.
- Class 3. Interpenetrated networks systems: where inorganic and organic polymeric networks are independently formed without mutual chemical bonds. The incorporation of inorganic macro-molecular networks into organic polymer structures is an example of this category.

- Class 4. Truly hybrids systems: where inorganic and organic polymeric systems with mutual chemical bonds are formed. These true hybrids have been specifically explored successfully for the development of new binders for use in high technology coatings.
- Class 5. Inorganic core/shell matrix systems: where, the potential and ability of the core/shell nanoparticles to obtain structures with combinations of the properties that neither individual material possesses is in consideration. The incorporation of inorganic core-shell ZnO-SiO₂ networks into organic polymer structures is an example of this category.

In this context, referring to the above cited category of the Inorganic-organic hybrid materials, some of the inorganic –organic hybrid nanocomposites materials which we have studied during the near past years will be explained

2. Class 1. Inorganic matrix systems

2.1 Synthesis of hydroxyapatite nanocomposites

The first group of inorganic-organic hybrids nanocomposites studied in our laboratory was in situe biomimetic synthesis of hydroxyapatite (nHAp) nanocomposite in simulated body fluid (SBF) at room temperature [17-19]. The synthesized hydroxyapatites with bone-bonding properties were widely used in hard tissue replacement due to their biocompatibility and osteoconductive properties. But the brittleness of HAp materials limits their use. One of the proposed methods to solve the problem was combination of HAp matrix (inorganic) with different organic polymers, such as collagen, wheat starch, gelatin and starch-gelatin mixture (organic). These natural biopolymers which are biodegradable, biocompatible, water soluble and inexpensive in comparison to the other biodegradable polymers, can be considered as a good candidate to impart suitable biological and mechanical properties to the synthesized nanocomposites. The effect of biopolymer template and its influence on the final morphology of nHAp has been revealed in this work via formation of rod like nHAp with about 6-12 nm width and 45-85 nm length (Fig. 1-2), in similarity with bone like material in human body. The shape of HAp crystals in a natural bone is needle-like or rod-like in 40-60 nm length, 10-20 nm width, and 1-3 nm thickness (Kikuchi et al., 2001; Mollazadeh, et al., 2007; Ramakrishna et al., 2001; Toworfe et al., 2006). The morphology and behavior of in vitro cultured BMSCs on n-HAp/starch nanocomposite was investigated under phase-contrast microscope and MTT assays evaluation. Fig. 2a-c presents phase-contrast micrographs of the cell attachment on HAp/0.5 g and nHAp/0.8 g starch biocomposite after culturing for 1, 3 and 7 days. At first day, recognition of elongated fusiform of BMSCs was too hard. After 3 days, a few BMSCs cells were present and after 7 days, a large amount of the proliferated cells, forming cell colony, were fully attached to the biocomposite. This observation, obviously showed that, n-HAp/ starch composite has no negative effect on the cell morphology, viability and proliferation. In MTT assays, starch and n-HAp /3.1 g starch composite were used to culture BMSCs for 1, 3 and 7 days, therewith a culture without biocomposite or biopolymer was used as blank control group. From the data in Fig. 3, the cell number was increased with the culture time on all tested groups. At the first and third day, there were no significant differences between absorbance values of the samples. While, after 7 days, the cells on biocomposite and control group were proliferated rapidly. As it can be find from this data, BMSCs cultured on biocomposite have much more proliferation compared to the gelatin in all the periods of time. The result shows that the presence of n-HAp in the composite has obvious effect on the proliferation of BMSCs.



Fig. 1. TEMimage image of HAp nanoparticles synthesized in absence (a) and presence of 0.8 g starch (b).



Fig. 2(a-c) presents phase-contrast micrographs of the cell attachment on the nHAp /0.8 g starch biocomposite after culturing for 1, 3 and 7 days.



Fig. 3. MTT assays for proliferation of BMSCs combined with gelatin, nHAp/0.5 g and nHAp/0.8 g starch cultured for 1, 3 and 7 days, compared with the control under the same culture condition.

3. Class 2. Organic matrix systems

3.1 Preparation and characterization of Ag/PVA nanorods by chemical reduction method

As an example for second category of inorganic-organic hybrid nanocomposites, silver nanorods was prepared in our laboratory with the average length of 280 nm and diameters of around 25 nm via a simple reduction process in the presence of polyvinyl alcohol (PVA, Mw=72,000) as solvent and protecting agent (Sadjadi et al., 2008). In this process, DMF has been served both as reductant and solvent. In the real reaction, two processes may be occurred simultaneously. At first, Ag nanoparticles are formed through homogenous nucleation and grow into multiply twinned particles (MTPs) with their surfaces bounded by the lowest energy {111} faces and then, *silver nanoparticles forming at the surface of the protecting agent or coming from the outer solution phase through Brownian motion aggregate into a 1D arrangement like a bunch of pearls, and grow into nanorods through Ostwald ripening.*

X-ray diffraction (XRD), Scanning electron microscopy (SEM), Transmission-electron microscopy (TEM) and UV-Vis spectroscopy techniques were used to characterize the prepared samples. It was found out that both temperature and reaction time are important factors in determining morphology and aspect ratios of nanorods. The TEM images of asprepared Ag nanorods by the controlled-concentration and temperature are shown in Fig. 4(a,b), revealing the as prepared individual Ag nanorods and their constituent nanospheres. Fig. 4(c) exhibits the cross section of the multiply fivefold twinned fcc Ag prepared crystallite. High concentrated distribution of Ag/PVA nanorods is observable on the SEM images (Fig. 5). The UV-visible spectrum of as prepared Ag/PVA nanorods showed a broad absorption band at λ max 458 nm. This characteristic peak was due to the oscillation of conduction band electrons of Ag known as the surface plasmon resonance (Cepak et al., 1998; Foss et al., 1994), (Link et al., 1999; Itakura et al., 1995; Jana et al., 2001). The position of plasmon absorption band (Khanna et al., 2005) was dependent of particle size, aspect ratio and diameter of nanorods and the broad nature of the absorption band in this case is indicative of the presence of both nanospheres and nanorods as reported in citrate reduction method (Zhou et al., 2006).



Fig. 4. Transmission electron microscopy (TEM) images of (*a*, *b*) individual nanosphere and nanorod crystals (c) cross section of Ag nanorods embedded in PVA.



Fig. 5. (a, b, c) SEM image showing high concentrated distribution of Ag/PVA nanorods.

4. Class 3. Interpenetrated network (IPN) system

4.1 Preparation of silicon based polymeric coatings

The sol gel process is used to produce silicon-based polymeric structures as interpenetrating networks in organic binder systems. Conditions for eligibility to participate in an interpenetrated nanocomposite are as follows: the two polymers have to be synthesized in the presence of each other, the two monomers should have the similar reaction kinetics, and the resulting materials should not to be phase separated. Interpenetrated polymer network (IPN) synthesized in this work was composed of an organic phase (GY250 = diglycidyl ether of bisphenol), an aromatic amine like HY850 and an inorganic silica phase formed by sol-gel process from TEOS and was coated on the aluminum alloy (AA) substrate by dip coating method (Rahimi et al., 2005; Sadjadi et al., 2009). The hybrid network obtained in this manner has an excellent optical transparency and was characterized using different spectroscopic and microscopic techniques. A significant feature in formation of this hybrid network to enhance compatibility with hybrid materials is formation of covalent bonding between organic polymers and inorganic compounds (Matejka et al., 2000). All modification

of the structures of the molecular species and the new bonds formed or destroyed during the sol-gel process were studied by using FTIR spectroscopy. The results showed formation of the Si-O-C bonds during the reaction and opening the epoxy ring (the peak of epoxy group disappeared). The SEM micrographs (Fig. 6) showed well dispersed of small particles with the average particle size diameter of 20-70 nm. The Si mapping image of hybrid inorganic-organic coating on the aluminum substrate after curing showed uniform distribution of Si nanoparticles (Fig. 7).



Fig. 6. The SEM image of inorganic-organic hybrid polymer on aluminium substrate after curing





4.2 Preparation of metallophthalocyanines on γ alumina support

Example of this category of inorganic-organic hybrid nanocomposite which we have prepared in our laboratory was metallophthalocyanines supported on γ -alumina as an effective

heterogeneous catalyst for oxidation of alcohols such as cyclohexanol, benzyl alcohol and hexanol (Lorber et al., 1996; Sadjadi et al., 2010; Sugimoto et al.,1985). Metallophthalocyanine (MPc) complexes have been used as alternative catalyst, because they have a similar structure to porphyrins and are cheaper, more stable to degradation *with higher catalytic performance*. Its incorporation with the solid supports for synthesis of heterogeneous catalysts is highly desirable (Geraskin et al., 2008; Sharma et al., 2003). The catalysts was prepared by dispersing MPc complexes (M= Fe, Mn and Co) into the already prepared γ -alumina. Formation of independent catalysts components have been confirmed and characterized by using X-ray diffraction (XRD), Scanning Electron Microscopy (SEM), Fourier Transform Infrared (FTIR) and UV-vis spectroscopy. Investigation on improvement of the catalytic activity of the prepared catalyst (MPc (Me= Fe, Mn and Co) complexes/ γ -alumina) in comparison with MPc (Me= Fe, Mn and Co) complexes/ γ -alumina) in comparison with MPc

5. Truly hybrids systems

5.1 Preparation of hydrophilic nanocomposite coating

Research on *functional hybrid materials* has become one of the most rapidly developing fields of materials chemistry. In its most basic sense, a hybrid material is obtained by combining at least two components, commonly inorganic and organic, at the nanometer scale. Methods to synthesize inorganic-organic hybrid materials are often based on soft chemistry approaches, such as sol-gel processes, intercalation, exchange, or grafting. Considering the variety of combinations of components (and properties), inorganic-organic hybrids represent an intriguing class of materials with a large spectrum of applications. In this section we will focuses on the synthesis of functional inorganic-organic hybrid materials, on the elucidation of structure-property relationships, as well as on the organization of hybrid building blocks. In this purpose, based on epoxy resin and titanate as precursor, we have prepared hydrophilic inorganic-organic nanocomposite coating films on the glass substrate. Transparent hydrophilic nanocomposite films based on TiO₂ on glass substrates have high potentiality for practical applications such as mirrors, window glasses, windshields of automobiles, and so on. Hydrophilic property of the surface allows water to spread completely across the surface rather than remaining as droplets, thus making the surface anti-fog and easy to wash. Their further characteristics were good mechanical properties (scratch and abrasion resistance) [53-59] and stability against wet climate conditions and UV radiation (Watanabe et al., 1996). This kind of hydrophilic coatings can be used in preventing dewdrops forming inside the windowpanes and greenhouses, for the purpose of protecting vegetables from rotting by dewdrops.

The films on the glass substrates were prepared by dip-coating process from a sol containing alcoholic tetrabutyl titanate which after the curing treatment, the gel forms a stable thin homogeneous nanocomposite coating. The films obtained were transparent to the visible light and their surface hydrophilicity values were increased by increasing TiO₂ nanoparticles content. Characterization of the nanocomposite coating films, performed by TEM showed that the particle size of the superposed TiO₂ nanoparticles in nanocomposite films were estimated about 2–4 nanometer (Fig. 8). Atomic Force Microscopy (AFM) observation showed uniformity and three-dimensional surface profile of TiO₂ nanospheres in the nanocomposite films (Fig. 9). The contact angle test without coating and after coating (Fig. 10), gave a good evidence for hydrophilicity of the prepared nanocomposite coatings and the strong interaction between organic and inorganic phase with the formation of titania domains in the nanoscale range. Applied humidity resistance test showed the high stability of nanocomposite coating in humidity exposure.



Fig. 8. TEM image of transparent hydrophilic inorganic-organic hybrid TiO_2 / epoxy resin hybrid coating film on glass substrate.



Fig. 9. AFM micrograph showed uniformity and a three-dimensional surface profile of TiO_2 nanospheres in the nanocomposite film.

6. Class 5. Inorganic core-shell matrix systems

In this category of the inorganic-organic hybrid coating, the ability and potential of the core/shell nanoparticles to obtain structures with combinations of properties that neither individual material possesses is in consideration. This category of core shell Inorganic – organic nanocomposite, due to the ease of manipulation of the nanoparticle morphologies, compositions and surface properties to earn the name of particle engineering, has attracted a lot of attention. It basically involves tailoring the surface properties of particles with a shell of controlled composition. The shell can alter the charge, functionality, and reactivity of the surface, or improve the stability and dispersive ability of the core. Furthermore, magnetic, optical, or catalytic functions can be imparted to the colloidal particles by the shell material. Spherical gold nanoparticles which have a Surface Plasmon Resonance at a wavelength of about 520 nm and a spherical silica core with a gold shell offering a very highly tunable Plasmon wavelength depending on the thickness of the shell and the core diameter is an example for this category of core shell nanocomposite.



Fig. 10. Transparent hydrophilic TiO_2 nanocomposite coating based on epoxy resin on glass substrate

6.1 Preparation of ZnO-SiO₂/Epoxy nanocomposites by sol-gel method

As a first example of this category of core-shell inorganic-organic hybrid materials, ZnO-SiO₂/Epoxy nanocomposites was synthesized in our laboratory by sol-gel process (YU et al., 2001). In this purpose, inorganic core shells of ZnO-SiO₂ were firstly prepared and embedded then in the organic polymeric networks. The morphology of the coating surface was elucidated by SEM and a mapping technique to investigate the dispersion of inorganic phase in the hybrid matrix. Figures 11 and 12 represent SEM photographs of pure glass without coating and inorganic core-shell ZnO/ SiO2/ epoxy hybrid nanocomposites coating. This image shows that the ZnO/ SiO2 particles were uniformly dispersed throughout the polymer matrix in nanometer sizes as well as good miscibility between organic and inorganic phases.



Fig. 11. SEM image of the surface of epoxy/polyethylene



Fig. 12. SEM image of the surface of Gy250/HY850/ GPTMS/ZnO-SiO2 nanocomposite film

6.2 Preparation and characterization of transparent SiO₂-Ag/PVP nanocomposit

As a second example of the core-shell inorganic systems, transparent SiO₂-Ag/PVP nanocomposite mirror films were prepared by sol gel method and characterized (Sadjadi et al., 2009). The results showed that, silica modified PVP is a remarkably powerful capping agent for preparation of 1D arrangement of Ag nanoparticles and this kind of prepared inorganic/organic nanocomposite can now be developed towards optical and medicinal based applications (Elechiguerra et al., 2005; Sondi et al., 2008; Suvorova et al., 2005; Zheng et al., 2001). The broad nature of the UV -Visible absorption band at λ_{Max} = 410 nm due to the oscillation of conduction band electrons of Ag indicated the presence of both embedded sphere and assembled nanospheres in SiO₂ modified PVP (Cepak et al., 1998; Jana et al., 2001; Link et al., 1999). Transparency dependent on the Ag nanoparticle size was about 96% in the infra-red region (Fig. 12, 13). The FTIR results indicated that the steric effect in the reaction between silver and PVP will be important when the particles size grow up upon curing of the sol and the main reaction between silver nanoparticles embedded in silica modified PVP may occur between O atoms of silica modified PVP and Ag nanoparticles. The XRD data confirmed that the Ag nanoparticles are crystalline with fcc structures having a preferred crystallographic orientation along the (220) direction. The grain size of the silver nanospheres estimated from the XRD peak width (and using Scherrer's formula), was about 8.4 nm.TEM observations from the side section of the prepared sample illustrated individual Ag nanosphere (Fig. 14) as well as self assembled nanosphere in a twinned wire like shapes with an average length of 200-250 nm and diameters of around 20-25 nm. TEM observations from side section of nanowires suggest that the transformation of Ag nanospheres to Ag nanowires is achieved by the oriented self assembling of the several spherical particles followed by their fusion. Resulting Ag nanowirs have a twinned fcc structure, and they appear in an cubic assemblage in fourfold twinning. SEM image of as prepared SiO₂-Ag/PVP nanocomposites illustrating homogenous mechanical mixture of the polymer and nanoparticles is given in Fig. 16.



Fig. 13. Transmittance spectrum of the as prepared core shell inorganic hybrid SiO2- Ag/PVP



Fig. 14. Transparent mirror coating of as prepared core shell inorganic hybrid SiO_2 -Ag/PVP nanocomposite films.



Fig. 15. TEM image of (a) Individual embedded Ag nanospheres assembled Ag nanosphere as a bunch of peals on the silica modified PVP, (b) side section of the Ag nanospheres crystallite assembly.



500nm

Fig. 16. SEM image of as prepared SiO2-Ag/PVP nanocomposites illustrating homogenous mechanical mixture of the polymer and nanoparticles.

7. Summary

Class 1. Inorganic matrix systems:

- HAp nanocomposite synthesis can be performed at room temperature by a mimetic method using wheat starch as a template agent.
- Controlling the shape and size of HAp nanoparticles is possible by choosing appropriate template and wheat starch is a good example.
- The effect of wheat starch template and its influence on the final morphology of nHAp is revealed via formation of rod-like nHAp with about 6–12nm width and 45–85nm length. The crystal shape of
- Morphology of the synthesized HAp using starch as a template is similar to the inorganic phase of human natural bone.
- In vitro bioactivity of the synthesized nHAp at the presence of wheat starch biopolymer is confirmed by formation of a layer of carbonated apatite on the surface of synthesized HAp after soaking them in SBF solution.
- The presence of n-HAp in the composite has obvious effect on the proliferation of BMSCs.

Class 2. Organic matrix systems:

- Polyvinyl alcohol (PVA) is a remarkably powerful capping agent for Ag ions.
- Di methyl formamide (DMF) is an appropriate solvent and reductant agent for the preparation of silver nanoparticles.
- Controlling the shape and size of silver nanoparticles by choosing an appropriate capping agent and solvent at ambient temperature is possible.
- Recorded UV-visible spectra indicated well-defined absorption bands for Ag nanoparticles or nanorods due to the surface plasmon resonance phenomena.
- The XRD patterns confirmed that the Ag nanorod is crystalline with fcc structure having a preferred crystallographic orientation along {2 2 0}direction, and a straight, continuous, dense Ag nanorod has been obtained with a diameter of 25 nm.
- SEM and TEM observations along a series of relevant directions showed that the silver nanorods have an average length of 280 nm and diameters of around 25 nm.
- TEM observations from cross section of nanorods suggested that the transformation of Ag nanospheres to Ag nanorods is achieved by oriented attachment of the several spherical particles followed by their fusion.
- Resulting Ag nanorods have a twinned fcc structure, and they appear in a pentagonal shape with fivefold twinning. The fivefold axis, i.e. the growth direction, normally goes along the (110) zone axis direction of the fcc cubic structure

Class 3. Interpenetrated network system:

- In this category of organic-inorganic hybrid system, the organic phase was composed of GY250 (diglycidyl ether of bisphenol A) and HY850 (aromatic amine); and an inorganic silica structure was formed by sol-gel process.
- The organic-inorganic hybrid material (nanocomposite) was coated on the aluminum alloy (AA) substrate by dip coating method.
- Obtained hybrid network coatings possess excellent optical transparency.
- ²⁹Si NMR spectrometry elucidated the type of formed molecular species and their structure.

- The modification of the structures of all molecular species and the bonds formed or destroyed during the sol-gel process were endorsed by using the FTIR spectroscopy.
- Formation of Si-O-C bond during the reaction and opening the epoxy ring was confirmed by FTIR spectra.
- Thermal stability of the prepared coating samples was confirmed by using TGA.
- SEM micrographs show that the Small dispersed particles of 20-70 nm diameter have been shoved by SEM micrographs.
- Preparation of metallophthalocyanines on γ -alumina support
- Metallophthalocyanines encapsulated in γ -alumina nanoparticles were directly synthesized by addition of the metal salt, phthalonitrile, urea and ammonium heptamolybdate to the γ -alumina'
- Cobalt, iron and manganese phthalocyanines incorporated with *γ*-alumina pores proved to be active, efficient and reusable catalysts for oxidation of various alcohols with good conversion percentage and 100% selectivity.

Class 4. Truly hybrids systems

- Preparation of hydrophilic nanocomposite coating
- Transparent hydrophilic organic-inorganic nanocomposite hybrid coating films based on epoxy resin were prepared using tetrabutyl titanate by a simple sol-gel method.
- Suitable conditions to obtain a complete conversion for preparation of the nanocomposite coatings, at a molecular level were established.
- The films were prepared on the glass substrates by dip-coating from a sol containing alcoholic tetrabutyl titanate which after the curing treatment, the gel forms a stable thin homogeneous nanocomposite coating.
- Obtained films were transparent to visible light and their surface hydrophilicity values were increased by increasing TiO₂ nanoparticles content in the water damp permeable self leveling flooring system.
- Characterization of the nanocomposite coatings performed by TEM showed that the size of the superposed TiO₂ nanoparticles in nanocomposite films were estimated about 2–4 nanometer.
- AFM observation showed uniformity and a three-dimensional surface profile of TiO₂ nanospheres in the nanocomposite film.
- The contact angle test without coating and after coating, gave a good reason for hydrophilicity of the nanocomposite coating and the strong interaction between organic and inorganic phase with the formation of titania domains in the nanoscale range.
- Applied humidity resistance test showed the high stability of nanocomposite coating in humidity exposure.

Class 5. Inorganic core-shell matrix systems:

- Preparation of ZnO-SiO₂/Epoxy nanocomposites by sol-gel method
- Thin film inorganic-organic hybrid coatings was successfully produced by sol-gel method reacting of GLYMO/ZnO-SiO2/EPOXY/aromatic (diglycidyl ether of bisphenol A) and HY850 (aromatic amine)/ PEG surfactance at room temperature.
- The optically transparent Prepared films were resistance to cracking, with excellent adhesion properties.

- The FTIR spectra confirmed formation Si-O-Si and Si-O-C, Zn-O-Si bonds and epoxy ring opening during the process.
- The Si mapping image confirmed uniformly distribution of dispersed inorganic nanoparticles in hybrid nanocomposites, which results in the formation of transparent coatings.
- Anti-fog coatings were prepared by incorporating PEG and surfactant to siliceous precursors.
- Hydrophilic properties of the surfaces were verified by contact angle measurements.
- Hydrophilic OH groups can be introduced in the hybrid system through chemical bonds, leading to an improvement of the wetting behavior without a change in the adhesion properties.
- It was shown as the amount and molecular weight of the added PEG, and surfactant is increased there is an obvious increase in hydroxyl content and the higher the hydroxyl content, the lower contact angel for water of the hydrophile nanocomposite coatings. SEM show the small dispersed particles which are aggregated in larger irregular aggregates of nano size.
- Preparation and characterization of transparent SiO₂-Ag/PVP nanocomposite:
- A transparent mirror films of inorganic/organic hybrid of SiO₂-Ag/PVP has been prepared by sol gel method.
- Silica modified PVP is a remarkably powerful capping agent for preparation of 1D inorganic-organic nanocomposite coating.
- Inorganic-organic transparent mirror films can be developed towards optical and medicinal based applications.
- The broad nature of the UV-Visible absorption band at λ_{Max} = 410 nm due to the oscillation of conduction band electrons indicated the presence of both embedded sphere and assembled nanospheres in SiO₂ modified PVP.
- Transparency of the prepared mirror films was dependent of Ag nanoparticle size and was about 96% in the infra-red region.
- FTIR results indicated importance of the steric effect in the reaction between silver and PVP when the particles size grow up upon curing of the sol.
- The main reaction between silver nanoparticles embedded in silica modified PVP was occrred between O atoms of the silica modified PVP and Ag nanoparticles.
- The XRD data confirmed that the Ag nanoparticles were crystalline with fcc structures having a preferred crystallographic orientation along (220) direction.
- The grain size of the silver nanospheres estimated from the XRD peak width (and using Scherrer's formula), was about 8.4 nm.
- TEM observations from of the side section of prepared samples illustrated individual Ag nanosphere as well as self assembled nanosphere in a twinned wire like shapes with an average length of 200-250 nm and diameters of around 20-25 nm.
- TEM observations from side section of nanowires suggest that the transformation of Ag nanospheres to Ag nanowires is achieved by the oriented self assembling of the several spherical particles followed by their fusion.
- Resulting Ag nanowirs have a twinned fcc structure, and they appear in an cubic assemblage of fourfold twinning.
- SEM image of as prepared SiO₂-Ag/PVP nanocomposites illustrated homogenous mechanical mixture of the polymer and nanoparticles .

8. Conclusion

In this work, a very simple and logic classification based on the morphological combinations of the inorganic –organic hybrid components were considered to study some limited examples of Inorganic-organic coating systems. We think that, it is still very soon to give some road maps to design and achieve a new inorganic –organic hybrid nanocomposite material with some proper properties.

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Synthesis and Analytical Applications of Quantum Dots Coated with Different Generations of DAB Dendrimers

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1. Introduction

Quantum dots (QDs), also known as luminescent nanocrystals, are a special class of semiconductors that possesses remarkable fluorescence emission properties (Coe et al., 2002; Tessler et al., 2002). Due to their unique optical characteristics, which include sharp emission spectra, QDs have been utilized for fluorescent tagging applications, demonstrating the advantages of high photobleaching threshold, good chemical stability, and readily tuneable spectral properties (Lebedkin et al., 2003; Hartschuh et al., 2003; Li et al., 2007; Leitão et al., 2008; Gonçalves et al., 2009). QDs have semiconductor properties different from bulk material due to the quantum confinement effects on their molecular band structure (Chen et al., 2003).

The synthesis, modification, and applicability of cadmium chalcogenide nanocrystals, in particular cadmium sulfide (CdS), have been optimized (Alivisatos, 1996; Weller, 1993). The interaction of the CdS nanocrystals with its environment or capping agent plays crucial role in determining its photoluminescent properties and reactivity (Aldana et al., 2001; Talapin et al., 2001; Wuister & Meijerink, 2003a,b; Uchihara et al., 2005; Chen & Rosenzweig, 2002). Polymer coating of QDs, rendering them biocompatibility and biostability, confers an important biomedical role in diagnostics and biochemical sensing (Pileni et al., 1992; Gattas-Asfura & Leblanc, 2003; Gao et al., 2008). Dendrimers are a particularly interesting class of emerging nanopharmaceuticals that can be used as capping agents of QDs.

Diaminobutane-based poly(propyleneimine) dendrimers (DAB) (Fig. 1) have been synthesised (Etienne et al., 2005) and applied for *in vitro* diagnostics (Schatzlein et al., 2005; Bawarski et al., 2008; Hezinger et al., 2008; Dutta et al., 2008) tested in preclinical studies as contrast agent for nuclear magnetic resonance (Kobayashi et al., 2003; Talanov et al., 2006). There are attempts to use dendrimers in the targeted of delivery of drugs and other therapeutic agents (Crampton & Simanek, 2007). Drug molecules can be loaded both in the interior of the dendrimers as well as attached to the surface groups (Liu et al., 2000; Fernández et al., 2006) and used as therapeutic agents, for example in cancer treatment (Hollins et al., 2004; Svenson & Tomalia, 2005). Besides biomedical applications, dendrimers can be used to improve many industrial processes. The combination of high surface area and high solubility makes dendrimers useful as nanoscale catalyst (Yu et al., 2008). The high potential of these compounds opens new perspectives to

bioimaging diagnosis (Scott et al., 2005), photosensors (Hezinger et al., 2008) of heavy metals (Bawarski et al., 2008) and organic pollutants (Lubick, 2009) and in detection of fingerprints in forensic chemistry (Juan et al., 2008).



Fig. 1. Molecular structure of different generations DAB dendrimers [DAB-dend-(NH₂)_n]; a) n=8 (generation 2-G₂); b) n=16 (generation 3-G₃); c) n=32 (generation 4-G₄); d) n=64 (generation 5-G₅).

The most used dendrimer for QDs capping is poly(amidoamine) (PAMAM) polymer. CdS-QDs and/or ZnS-QDs have been synthesized using dendrimer structure, where polyamide dendrimer (PAMAM) is employed as host confinement (Juan et al., 2008; Sooklal et al., 1998; Wisher et al., 2006; Ling & Cong, 2008). Hybrid CdS DAB dendrimer nanocomposite have been synthesised and characterized in methanol (Lemon & Crooks, 2000; Gayen et al., 2007). These nanocomposites are formed by the arrested precipitation of nanometer-scale CdS clusters in the presence of polyamide dendrimers. Although we do not yet know the exact locus of cluster nucleation, the dendrimer clearly interacts with the clusters at a relatively early stage in the arrested precipitation, retarding further growth and producing small QDs clusters with unique photoluminescent properties. The dendrimer scale composite flocks. Despite this aggregation, the long term stability of the materials and its photoluminescent properties suggests that the QDs clusters do not coalesce but remain as distinct entities (Hedden et al., 2002; Huang & Tomalia, 2005).

A severe limitation of the biomedical or biochemical *in vivo* imaging applications of cadmium chalcogenide QDs is their potential cytotoxicity due to the release of cadmium ions. Moreover, hybrid dendrimer QDs nanocomposites are usually synthesised and kept in organic solvents, like methanol, which are toxic or bioincompatible. In order to reduce or eliminate health risk, cadmium ions should be replaced with other less or no toxic metal

ions like zinc and these nanoparticles should be synthesised and kept in aqueous media, *i.e.* using a green chemistry approach.

In this chapter, the simple aqueous synthesis and characterization of hybrid nanocomposites constituted by CdS, ZnS and CdS/ZnS-QDs and different generations (from 2 up to 5) of DAB dendrimer is presented. Moreover, the application of these nanocomposites as nanosensors of Hg(II) ion, pH, ionic strength and nitromethane is described.

2. Aqueous synthesis of the nanocomposites

2.1 Materials

Polypropylenimine tetrahexacontaamine dendrimer, generations 2 to 5 (DAB- $G_{n\nu}$ n=2-5) (Fig. 1), cadmium chloride (CdCl₂, 99.9%), zinc chloride (99.9%) sodium sulphide (Na₂S·9H2O) were purchased from Sigma-Aldrich Química S.A. (Spain) and 3-mercaptopropinoic acid (MPA, 99%) from Fluka. Standard aqueous solutions of Hg(NO₃)₂, Pb(NO₃)₂, CdCl₂, Cu(NO₃)₂, NiCl₂, CoCl₂ and Zn(NO₃)₂·4H₂O and nitromethane were obtained from Merck. All solutions were made with deionised water with resistivity higher than 4 MΩ/cm.

2.2 Synthetic procedures

2.2.1 Synthesis of DAB-CdS QDs

DAB dendrimer of different generations (DAB- G_n =2-5) (10.0 mg) from Aldrich, were dissolved in 20.0 mL in deionised water and stirred for 24 hours. After that, CdCl₂ (Aldrich) was added to the solution for a DAB- G_n =2-5:Cd molar ratio of 1:10 and left to stabilize for 24 hours. 100 µL of MPA was added and left to stabilize for 24 hours (Belcastro et al, 2004). Na₂S·9H2O was then added with a Cd:S molar ratio of 1:1, and stirred for 72 hours to obtain an aqueous solution that was centrifuged at 13000 rpm for 10 min. Then, the solid obtained was washed with water and acetone, freezed and lyophilized. When no precipitate was detected the aqueous solution was dialyzed for 12 hours against deionized water using a MW CO 12.000-14.000Da dialysis tube (Medicell International).

2.2.2 Synthesis of DAB-CdS:ZnS QDs

This synthesis followed the same procedure previously described, except for $DAB-G_n(=2-5)$:Cd:Zn molar ratio that was 1:5:5.

2.2.3 Synthesis of DAB-ZnS QDs

The synthesis followed the same sequence of dendrimer-CdS QDs synthesis, except the pH of the solution, adjusted to 12 with tetrabutylammonium hydroxide (TBAH) (Li et al, 2007) in 2-propanol/methanol after addition of MPA. Firstly, the additions of TBAH provoke the precipitation of zinc hydroxide, followed by redissolution as soluble zinc hydroxyl complexes.

2.3 Characterization procedures

Scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDS) were done on a FEI Quanta 400FEG/EDAX Genesis X4M high resolution Scanning Electronic Microscope at 15 kV. For SEM analysis of aqueous dendrimer-QDs, a microliter sample was evaporated under vacuum at room temperature, and solid dendrimer-QDs were immobilized on a carbon fiber, both were held on an aluminium support.

Absorbance measurements were made in a Hewlett-Packard HP8452A diode-array spectrophotometer using 1 cm pathlength quartz cuvettes.

Fluorescence confocal microscopy was used to record the luminescence spectra of solid samples, acquired with a Leica SP2 AOBS SE (Leica Microsystems, Germany). The excitation of solid dendrimer-QDs was made with the Ar laser lines of 458 and 476 nm. A filter-free prism spectrophotometer head with a set of 3 photomultiplier tubes (PMT) allowed the addressing of distinct detection channels in three user-defined spectral ranges. All the image processing operations were done with ORIGIN50 and LCS Lite

(http://taltos.stanford.edu/pages/cocoa_leica.htm).

Steady state fluorescence measurements of aqueous solutions of dendrimer-QDs photoluminescence were done with a Spex 3D Spectrofluorimeter with a 75W xenon lamp and a CCD detector. Raw EEM were acquired, in an excitation wavelength range from 296.4 to 675.1 nm, and in an emission wavelength range from 350.7 to 721.8 nm, with a resolution of 2 nm, slit of 0.25 mm and 1 s integration time. A 1 mL quartz microcell was used. Lifetime measurements were recorded with a Horiba Jovin Yvon Fluoromax 4 TCSPC using the following instrumental settings: 368 nm NanoLED; time range, 1.6 µs; peak preset; 10,000 counts; repetition rate, 500 kHz; synchronous delay, 25 ns; emission detection: 535 nm.

3. Characterization of the nanocomposites

3.1 Morphological properties

In order to confirm the elemental composition of the synthesised dendrimer-QDs nanocomposites EDS analysis were done and, as example, Fig. 2 shows the EDS spectra of DAB-G₂ with CdS (Fig. 2.a), ZnS (Fig. 2.b) and CdS:ZnS (Fig. 2.c). These spectra confirm that the synthesized nanocomposites are indeed DAB capped with CdS, CdS:ZnS and ZnS QDs. Indeed, the presence of the signals due to elements Cd, Zn and S confirm the composition of the QDs, C and N confirms that the synthesized material contains QDs capped with DAB. Also, the presence of signals due to the elements C, O and S suggests that MPA is capping QDs. These results suggest that the QDs are stabilized in water due to the capping of both the dendrimer and MPA.

Fig. 3 shows, as example, SEM images of DAB-G₂ with CdS (Fig. 3a), CdS:ZnS (Fig. 3.b) and ZnS (Fig. 3.c). Although SEM images could not give particularly useful information about the morphology of the synthesised nanocomposites, the analysis of these images usually shows macroscopic spherical structures on the surface topography of the nanocomposites. A general examination of all SEM analysis suggests an amorphous nanocomposites structure. Nevertheless, the analysis of some SEM images, where macroscopic spherical structures could be observed, reveals dimensions comprised between 320 to 735 nm.

3.2 UV-Vis absorption properties

UV-Vis absorption spectra of all the DAB-QDs nanoparticles in water are shown in Fig. 4. The analysis of these spectra shows the following:

i. DAB-CdS QDs (Fig. 4a) are characterized by a well defined shoulder in the range between 370 to 390 nm (DAB-G₅ - 370 nm; DAB-G₄ - 380 nm; and, DAB-G₃ - 390 nm). DAB-G₅-CdS QDs show another well defined shoulder at about 325 nm. Also, there is a blueshift of the absorption band as the generation of the dendrimer is increased. This result is similar to that described in the literature when methanol was used as solvent (Gayen et al., 2007). The absorption shift that is observed for the different generations of DAB confirms that the amine groups are participating with MPA in the capping of the QDs.



Fig. 2. EDS spectra of DAB-G₂-CdS (a), DAB-G₂-CdS:ZnS (b) and DAB-G₂-ZnS (c) nanocomposites.



Fig. 3. SEM images of: a) DAB- G₂-CdS; b) DAB- G₂-ZnS; and, c) DAB-G₂-CdS:ZnS.

- DAB-ZnS QDs (Fig. 4.b) are all characterized by a poorly defined shoulder in the range between 250 to 260 nm. This shoulder is barely detected in the spectra of DAB-G₂-ZnS QDs.
- iii. DAB-CdS:ZnS QDS (Fig. 4.c) are characterized by a well defined shoulder in the range 325 to 350 nm (DAB-G₅ 325 nm; DAB-G₄ 350 nm; and, DAB-G₃ 330 nm). DAB-G₅-CdS:ZnS QDs show another well defined shoulder at about 284 nm.

The absorptions of the DAB-CdS QDs and DAB-ZnS QDs are blueshifted from the expected values of bulk CdS and ZnS, respectively 510 and 335 nm (Unni et al., 2009). This result is a consequence of the quantum confinement effects in the nanoparticles confirming the existence of QDs. Also, the absorption wavelengths suggest that the sizes of the QDs are in the nanometers range (Gayen et al., 2007; Unni et al., 2009). The absorptions of the hybrid DAB-CdS:ZnS QDs occur at intermediate wavelengths of the absorptions of the single QDs. This hybrid system can be seen as Cd²⁺ doped DAB-ZnS QDs and the presence of Cd²⁺ provokes a redshift that has been previously described in the literature (Unni et al., 2009).

3.3 Steady state fluorescent properties

All the synthesized nanocomposites were fluorescent either in the solid or in aqueous solution. The fluorescence of the purified solid nanocomposites were analysed by confocal microscopy. Fig. 5.a shows, as an example, the confocal image of DAB-G₃-CdS:ZnS where the green fluorescence (emission at 525 nm) can be observed. Table 1 summarizes the maximum wavelength of the emission of fluorescence of the solid nanocomposites. The general trends in the maximum wavelength of emission are: (a) within the same DAB generation a blue shift is observed in the maximum emission of fluorescence when CdS QDs is replaced by ZnS QDs; (b) a blue shift in the maximum fluorescence emission is also observed when the DAB generation is increased.

The solid nanocomposites emit in the range between 483 nm (DAB-G₂-ZnS) up to 545 nm (DAB-G₂-CdS) with a relatively high emission full width of half maximum (FWHM) (between 113 to 165 nm) when compared with typical narrow emission bands of QDs. This relatively high FWHM suggests that the CdS and ZnS QDs show a high degree of size heterogeneity probably because they are bounded to different chemical environments of the DAB dendrimer. The asymmetrical dispersion of QDs on the surface and the inner of dendrimers show the possibility of DAB to have focal regions where QDs can easily be linked and deposited controlling the growth of QDs. Being nanosized structures, dendrimers may respond to stimuli from the surroundings and can, like proteins, adapt a tight-packed conformation ("native") or an extended ("denaturated") conformation, depending on solvent, pH, ionic strength and temperature (Ballauf et al., 2001).



Fig. 4. Absorption spectra of DAB-CdS (a), DAB-CdS:ZnS (b) and DAB-ZnS (c) in water synthesized using DAB- G_2 , G_3 , G_4 and G_5 dendrimers.





Fig. 5. Fluorescence emission image of DAB-G₃-CdS:ZnS obtained by confocal microscopy (a) and spectra of the three nanocomposites synthesized using DAB-G₄ (b).

	G ₂			G3				
	pН	λ_{ex}	λ_{em}	FWHM	pН	λ_{ex}	λ_{em}	FWHM
CdS_s	3.18		545	156				
CdS_{aq}					3.27	344	607	227
CdS:ZnS _s	3.19		545	165	3.40		525	163
CdS:ZnS _s					3.40	382	555	170
ZnS_s	12.00		483	129	12.06		476	113
ZnS_{aq}	12.00	353	441	140	12.06	342	451	142
			G_4			G_5		
	pН	λ _{ex}	λ_{em}	FWHM	pН	λ _{ex}	λ _{em}	FWHM
CdS_s								
CdS_{aq}	3.10	369	584	82	3.22	342	535	201
CdS:ZnS _s					3.22		485	146
CdS:ZnS _s	3.40	344	460	157	3.22	344	453	158
ZnS_s								
\mathbf{ZnS}_{aq}	12.02	342	443	140	12.04	333	431	132

Table 1. Fluorescence properties of the synthesized DAB-QDs nanocomposites.

The water soluble synthesized nanocomposites show similar fluorescence properties as the solid materials (Table 1). Fig. 5.b shows, as example, the fluorescence emission spectra of the three soluble DAB-G₄ nanocomposites. The same trends of the maximum emission wavelengths with the QDs type and DAB generation are observed. This last generation trend has already been described in the literature for diferent generations of DAB-CdS nanocomposites in methanol solution (Gayen et al., 2007). The aqueous solutions of nanocomposites emit in the range 431 mn (DAB-G₅-ZnS) up to 607 nm (DAB-G₃-CdS) with FWHM usually higher than the solid nanocomposites - a FWHM of 227 nm is observed for DAB-G₃-CdS.

The synthesized nanocomposites show similar emission maximum to literature reports of mercaptoacetic acid-capped-CdS (541 nm) (Wisher et al., 2006) and thioglycerol-capped-ZnS (411 nm) (Unni et al., 2009; Jie et al., 2007). Also, the synthesized CdS nanocomposites have similar emission spectral characteristics to those reported in the literature, namely broad spectra with maximum intensity wavelength in methanol solution at about 470 nm (Gayen et al., 2007).

The fluorescence properties of the synthesised nanocomposites can be slighly modified if the reaction conditions are changed. For instance, the fluorescence intensity of the material increases with the stirring time which is related to the agglomeration of conjugated DAB-QDs. The amino groups of the DAB surface have a tendency to link with another dendrimer molecules by hydrogen bonding (Nourse et al., 2000). The solvent, pH, ionic strength and temperature are the experimental factors that can change the conformation and assembly of dendrimers (Ballauf et al., 2001). Maintaining the same chemical and physical conditions, the fluorescence intensity increases up to nearly 72 h and then decreased due to a high molecular density that cause the increasing of stereochemical repulsions leading to the split of agglomerated dendrimers.

3.4 Fluorescence lifetime analysis

A typical fluorescence time decay profile of the nanocomposite DAB-G₅-CdS is shown in Fig. 6. The time decay is complex showing the presence of lifetime ranges from the picoseconds and up to almost the microseconds. However, a four component decay time model originated a good fit ($\chi = 1.20$) with the following lifetimes: $\tau_1 = 657$ ps; $\tau_2 = 10.0$ ns; $\tau_3 = 59.42$ ns; and $\tau_4 = 265$ ns. The existence of relatively long lived components in dendrimer stabilized QDs (in the range of τ_3 and τ_4) has already been observed in studies using methanol as solvent (Lakowicz et al., 1999; Gayen et al., 2007).

4. Applications of the DAB nanocomposites as nanosensors

The nanocomposites constituted by a dendrimer (DAB), a capping agent (MPA) and QDs show several reactive sites that make them potential chemical sensors. Indeed, both the dendrimer and the capping agent have ionisable and metal complexing groups and the dendrimer can undergo structural modifications as consequence of the presence of organic molecules soluble in water or ionic species. These modifications on the physico-chemical environmental surrounding the QDs will affect their fluorescence emission properties because it will provoke modifications on the quantum confinement regime. In this section the nanocomposite DAB-G₅-CdS will be used to demonstrate that these nanomaterials can be used as nanosensors for pH, mercury(II) ion [Hg(II)], ionic strength and nitromethane.



Fig. 6. Fluorescence time decay of fluorescence of aqueous solution of DAB-G5-CdS.

4.1 Sensing the pH

The effect of the pH (range of pH between ca. 3 and 9) on the fluorescence intensity of aqueous solutions of the DAB-G₅-CdS nanocomposites is shown in Fig. 7. A detailed analysis of this effect of the pH shows the existence of a marked fluorescent intensity decrease in the pH range from 5 to 7 and a relatively small increase for pH values higher than 7 (Campos et al, 2009). Also, a blue shift is observed from 518 to 500 nm as the pH increases. These variations are a consequence of the change of the quantum confinement of the QDs as consequence of the ionization of the carboxylic groups of MPA and amine groups of DAB capping the CdS QDs (Gonçalves et al., 2009; Leitão et al., 2008).

The variation of the fluorescence properties (intensity and wavelength at the maximum of the emission spectra) of DAB-G₅-CdS with the pH was expected because QDs capped with ionisable ligands are quite promising pH sensors (Maule et al, 2010). However, when the



Fig. 7. Emission spectra of DAB-G5-CdS at different pH values.

QDs is attached to DAB other applications can be designed taking into consideration the unique properties of dendrimers.

4.2 Sensing Hg(II) ion

The effect of the Hg(II) ion on the fluorescence intensity of aqueous solutions of the DAB-G₅-CdS nanocomposites is shown in Fig. 8. This figure shows a marked quenching of the fluorescent intensity with the increase of the Hg(II) concentration without wavelength shift of the emission band (Campos et al, 2009). The analyze of the quenching mechanism provoked by Hg(II) ion was done using Stern–Volmer plots which show a static quenching with a Stern–Volmer constant for Hg(II) was 1.5×10^{-5} M⁻¹. This result suggests the formation of a quite stable complex between the DAB-G₅-CdS nanocomposites and Hg(II) ions.



Fig. 8. Emission spectra of DAB- G_5 -CdS without and in the presence of increasing Hg(II) ion concentration.

The effect of micromolar concentration of the metal ions Pb(II), Cd(II), Zn(II), Cu(II), Co(II) and Ni(II) on the DAB-G₅-CdS nanocomposite fluorescence has also been analysed and only Pb(II) and Cu(II) provokes measurable quenching (Campos et al, 2009). The Stern–Volmer constant for Cu(II) was 1.9×10^5 M⁻¹ and for Pb(II) 2.2×10^4 M⁻¹.

4.3 Sensing the ionic strength

The effect of alkaline metal ions in the molar concentration range (ionic strength effect) on the wavelength of the maximum of the emission spectra of aqueous solutions of the DAB- G_5 -CdS nanocomposites is shown in Fig. 9. This figure shows a marked redshift with the increase of the ionic strength (Campos et al, 2009).

Varying the ionic strength has a strong effect on charged DAB dendrimers and favours a contracted conformation with a high degree of back-folding somewhat similar to what is observed upon increasing pH or poor salvation (Welch and Muthukumar, 1998; Ramzi et al., 2002; Campos et al, 2009). This conformation changing provokes a modification of the chemical environment surrounding the QDs affecting the corresponding emission of fluorescence properties.

4.4 Sensing nitromethane

The effect of the nitromethane on the fluorescence intensity of aqueous solutions of the DAB-G₅-CdS nanocomposites is shown in Fig. 10. This figure shows a marked quenching of the fluorescent intensity with the increase of the nitromethane concentration without wavelength shift of the emission band (Campos et al, 2010). The analyze of the quenching mechanism provoked by nitromethane was done using Stern-Volmer plots which show a dynamic quenching with a Stern-Volmer constant of 25(6) M^{-1} and a percentage of fluorophores accessible to the quencher of about 81%. This result shows that about 19% of the QDs (fluorophores) attach to the dendrimer are located in the inner layers of the dendrimer while about 81% are located in the external layer (Campos et al, 2010).



Fig. 9. Maximum wavelength of the emission spectra of DAB-G₅-CdS in the presence of increasing potassium chloride concentration.



Fig. 10. Emission spectra of DAB-G₅-CdS without and in the presence of increasing nitromethane concentration.

5. Conclusions and perspectives

This chapter described the successfully aqueous synthesis of hybrid nanocomposites of CdS, ZnS and CdS:ZnS QDs with different DAB dendrimer generations. Aqueous solutions of DAB-ZnS QDs based nanocomposites show absorption in the 250 to 260 wavelength range and a fluorescence emission in the 430 to 450 nm wavelength range (a Stokes Shift about 200 nm). Consequently stable water solutions of DAB-ZnS QDs nanocomposites could be obtained which are less toxic than the other cadmium based QDs methanol solutions. The synthesis of this stable, low toxic, high luminescent dendrimer based nanocomposites, opens new potential applications to this family of substances.

As shown in this chapter quite interesting applications of the DAB-QDs nanocomposites as nanosensors can be designed using different strategies. Indeed, the following approaches were observed:

- i. pH sensors can be developed taking advantage of the ionisable functional groups;
- ii. the metal ion coordinating ligands of the dendrimer and/or QDs capping agents can be used for metal ions sensing;
- iii. the collision of a quencher with the external layer of the dendrimer can deactivate the fluorescence of the fluorophore (QDs) and constitutes the bases for the development of the sensor for the quencher;
- iv. reorganization and/or modification of the dendrimer structure around the fluorophore (QDs) can be used as a sensor for example for the ionic strength.

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Synthesis, Structural and Thermal Properties of Nano-porous SiO₂-based Aerogels

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1. Introduction

Nano-porous silica aerogels are unique materials often having a high specific surface area, a high porosity (75-99%), a low thermal conductivity (0.01-0.03W/mK), and a low index of refraction. Because of their unique properties, aerogels have been extensively studied, not only for use as transparent thermal insulators but also as inter-metal dielectric materials, optical and acoustic applications, and the space industry (Muller et.al, 1999; Hrubesh et.al, 2001;Kim & Hyun,2003;Lu et.al,1991). NASA has applied aerogel on the Mars Pathfinder Sojourner rover and Mars Exploration rovers for insulation purposes. Additional applications of aerogels are found in battery electrodes, catalysts and electronic devices (Fricke et.al, 1992; Fricke & Tillotson, 1997; Kuhn et.al, 1995; Chadwick et.al, 2001).

Currently SiO₂, Al₂O₃ and C aerogels are reported and available elsewhere. During the production of aerogel a wet gel is formed which dried becomes filled with air. An aerogel is made up of microscopic beads or strand chains connected to form a continuous network, it is considered a solid. The fact that typical aerogels have more than 90% porosity gives them unusual characteristics (Yoda et.al, 1998; Klementiev, 2001). Their structure is composed of a 3-D connected network of channels made of thin ligaments. The thickness of ligaments determines the final density and porosity of the aerogel (Reim et al, 2004; Kwon & Choi, 2000).

As for thermal insulation application, generally monolithic SiO₂ aerogels provide a whole low thermal conductivity due to its extremely high porosity. The thermal conductivity of aerogels is about 100 times smaller than that of full density silica glass, although Kistler made initial thermal conductivity measurements, a detailed understanding of thermal transport in aerogel resulted from investigations carried out (Fricke & Tillotson, 1997). Thermal transport in aerogel occurs via gaseous conductivity, solid conductivity and infrared radiative transfer. Usually at room temperature, aerogels have a low thermal conductivity due to its special gas conduction and solid conduction. However, at higher temperatures, radiative absorption/emission becomes the dominant heat transfer mechanism.

Monolithic aerogel behaves poor thermal insulation because it is highly transparent in the 3- 8μ m wavelength region. To improve its thermal insulation capacity, approaches such as doping aerogel with carbon have been applied to minimize infrared radiation heat transfer. The specific extinction for C doped aerogels is drastically increased, especially in the 2 to

8μm range. Carbon black doped aerogel beads have total thermal conductivity of about 0.020 Wm⁻¹K⁻¹ in air, while for monoliths approximately 0.015 Wm⁻¹K⁻¹ holds(Zhang et.al,2009). The opacified fibers also suppress radiation transport by eliminating the infrared transparent window of aerogel and strengthen the brittle monolithic aerogel when fibers are incorporated into the aerogel matrix. Therefore, an appropriate selection of fiber type and concentration is critical to optimizing the thermal insulation capacity of the material, especially at high temperatures. K₂Ti₆O₁₃ whisker is an efficient opacifier due to its high-reflection index, thermal stability and negative temperature coefficient; therefore it drastically reduces the radiative heat transfer in the prepared SiO₂ aerogels. Additionally TiO₂ is also a good opacifier due to its high reflection index, thermal stability and strong broad band absorber. The specific extinction of the opacified aerogel is drastically increased, especially in the range from 2 to 8 μm (Wang, et.al, 1995).

2. Production of aerogels

2.1 Silica aerogels

Since the actual applications for aerogels are virtually unlimited, they will have to be cheaply manufactured in order to have an impact in the commercial marketplace. As such, many researchers have now paid their attention to achieving these goals. Some research institutions have designed methods to eliminate the supercritical dying process and the high capital cost associated with it, while others have began to make it more efficient. Practicing results have revealed that the high cost of the raw materials contributes significantly to the final cost of the aerogel.

Usually Silica aerogels were prepared by hydrolysis and polycondensation of solvent (alcohol) diluted alkoxide in the presence of a catalyst. The hydrolysis and polycondensation reaction mechanism for tetraethoxysilane (TEOS) precursor is as given below: Hydrolysis:

$$Si(OC_2H_5)_4 + 4H_2O \rightarrow Si(OH)_4 + 4C_2H_5OH \tag{1}$$

A catalyst (Critic acid) is used here. Condensation:

$$Si(OH)_4 + Si(OH)_4 \rightarrow \equiv Si - O - Si \equiv +4H_2O$$
⁽²⁾

$$Si(OH)_4 + Si(OC_2H_5)_4 \rightarrow \equiv Si - O - Si \equiv +4C_2H_5OH$$
(3)

Similarly, tetramethoxysilane (TMOS) and polyethoxydisiloxane (PEDS) precursors follow the same trend of chemical reactions. There are some structural differences among TEOS, TMOS and PEDS, although the reactive mechanism is similar during the process of hydrolysis and condensation. Figure.1 lists the pore size distribution using TEOS, TMOS and PEDS as precursors.

From the present studies, it has been found that the precursors: TEOS, TMOS and PEDS strongly affect the physical properties like bulk density, percentage of porosity, pore size distribution, optical transmission, surface area, thermal conductivity and microstructure of silica aerogels. Table.1 shows the effect of various precursors on some physical properties of silica aerogels.

Precursor	Optimized molar ratio: Solvent: water	Catalyst	Gelation time	Bulk density (Kg m ⁻³)	Porosity (%)	Surface area (m ² gm ⁻¹)	Thermal Conductivity (Wm ⁻¹ K ⁻¹)
TEOS	TEOS:EtOH:H ₂ O 1:5:7	Citric acid 0.001M	2.2days	230	87.89	800	0.060
TMOS	TMOS:MeOH:H ₂ O 1:12:4	NH4OH 0.05M	30min	129	93.21	1000	0.020
PEDS	PEDS:EtOH:H ₂ O 1:5:6	HF 0.01M	10min	98	96.84	1100	0.015

Table 1. Effect of various precursors on some physical properties of silica aerogels. Ref (Wagh, et al, 1999)

The experimental results showed that TMOS and PEDS aerogels has high surface areas of 1000 and 1100 m²gm⁻¹, respectively. While, TEOS aerogel possesses low (800 m²gm⁻¹) surface area compared to the TMOS and PEDS aerogels. This is due to the fact that both the TMOS and PEDS aerogels consist of smaller size SiO₂ particles of the network whereas TEOS aerogels consists of larger size SiO₂ particles of the network as explained earlier. The thermal conductivity of the TEOS aerogels measured at room temperature has been found to be 0.06 Wm⁻¹K⁻¹ whereas the thermal conductivity values for TMOS and PEDS aerogels have been found to be 0.02 and 0.015 Wm⁻¹K⁻¹, respectively. This is due to the fact that the density of the TEOS aerogel is higher (230 Kg m⁻³) compared to the densities of TMOS (129 Kg m⁻³) and PEDS (98 Kg m⁻³) aerogels. The dependence of thermal conductivity as a function of density is explained in the results.



Fig. 1. Pore size distributions (PSDs) of silica aerogels for various precursors: TEOS, TMOS and PEDS. Ref.(Wagh, et al, 1999)

Aerogels are often produced by the supercritical extraction of pore liquid from wet gels, which limits industrial-scale production of aerogels. Silica aerogels were recently prepared at an ambient pressure through solvent exchange and surface modification of wet gels. Solvent exchange and surface modification are essential to preserve the porous network of the gel before ambient pressure drying. Usually, under the condition of an ambient pressure dying, surface-modified agent is required. To modify the surface of the gel, a simultaneous solvent exchange and surface modification process at ambient pressure is needed to reduce the time required for synthesis from several days and to reduce shrinkage during drying.



Fig. 2. FE-SEM micrograph of (a) unmodified and (b) TMCS modified (10%V of TMCS) mesoporous silica beads. Ref (Sarawade et al, 2010)

Figure.2 shows the pore characteristics and structure morphology of mesoporous silica beads based on SEM micrographs of unmodified and 10%V TMCS modified silica beads. In general, the unmodified silica beads formed dense aggregates of spheres while the modified silica beads had highly porous structure. This is because the unmodified wet gel silica beads shrank more during ambient pressure drying, resulting in dense aggregates of dried silica beads and the loss of mesopores. The samples modified with TMCS had mesopores with an average pore diameter in the range of 8-13um. This is due to the fact that reversible shrinkage occurred in the wet gel silica during drying because of organic modification of the surface with trimethyl groups.



Fig. 3. Pore size distributions of (a) unmodified silica beads together with those modified with (b) 2 (d) 6 and (f) 10% V of TMCS. Ref (Sarawade et al, 2010)

Figure.3 shows the pore size distribution of unmodified and modified silica aerogels. Unmodified silica beads have a narrowpore size distribution with a peak pore diameter of 6.1 nm. Modified silica beads had a broad pore size distribution with the peak pore diameters ranging from 8 to 13 nm. The peak pore diameter increased as the volume of TMCS increased from 2 to 10%. This enlargement of pores is considered to be due to the increase in non-polar alkyl groups (-CH₃) on the silica surface, which reduces shrinkage during drying and therefore increases pore size. As per the IUPAC classification of pores, all the silica beads showed a pronounced peak in the mesopore region (2–50 nm) indicating that the mesopores in the modified silica beads have remained intact, even after the drying process.

During synthesizing SiO_2 aerogels, modification solvent plays an important role in determining the final microstructure. In our previous studies, cyclohexane was selected for surface modification of SiO_2 aerogel using TEOS as precursor before ambient pressure dying. Figure.4 showed the unmodified and modified micro-morphology using cyclohexane as solvent exchange. The unmodified silica aerogel formed some aggregates of spheres while the modified silica aerogel had porous structure with high porosity. These results might be identical to that of Ref(Sarawade et al, 2010).



Fig. 4. SEM micrograph of (A) unmodified and (B) cyclohexane modified mesoporous silica aerogels

2.2 Carbon aerogels

Carbon aerogels or porous carbons synthesized via the sol-gel route, are considered as very interesting materials for high-temperature thermal insulations in non-oxidizing atmospheres or vacuum (Pekala, 1989; Hrubesh & Pekala, 1994). Carbon aerogels are open porous solids consisting of a three-dimensional network of spherical interconnected primary particles. The mean pore and particle size can be specifically adjusted to be in the range from several nanometers only to some microns by varying the synthesis conditions. Porosities up to about 99% can be achieved. These properties make carbon aerogels suitable for thermal insulation applications (Li et.al, 2002; Petricevic et.al, 2001), in particular at high temperatures, but also for electrodes in supercapacitors and gas diffusion layers in fuel cells. Carbon aerogels are often produced using RF (resorcinol and formaldehyde as the main precursors) method. RF polymer precursor was prepared by polycondensation of resorcinol with formaldehyde in an aqueous solution. Sometimes, sodium carbonate, which was used as a base catalyst, was mixed with resorcinol and deionized water, to accelerate dehydrogenation of resorcinol. After stirring the solution for a few minutes, formaldehyde was added slowly into the solution to form a sol.



Fig. 4a. Overall preparation route for carbon aerogels Ref (Yoon Jae Lee et.al, 2010)

Yoon Jae Lee et.al (Yoon Jae Lee et.al, 2010) listed typical the processing route for carbon aerogels (see Figure.4a). M.Wiener et.al (Wiener et.al, 2009) investigated the high-temperature insulation properties of carbon-based aerogels derived via pyrolysis of organic aerogel precursors, which were synthesized using resorcinol and formaldehyde as

precursors according to the sol-gel process. The reactants resorcinol and formaldehyde in the starting aqueous solution was adjusted to a mass ratio M of 25% (M = mass of resorcinol and formaldehyde to total mass of the solution) to yield a density of the resulting aerogel of about 230 kg m⁻³. After carbon gel formed, the samples were exposed to 85°C for 24 h for gelling and curing. The pore liquid within the wet gel was replaced by ethanol to reduce the surface tension upon drying. Subsequently, the gels were dried at ambient conditions. Finally the resulting organic aerogels were pyrolyzed in an argon atmosphere at 1073K and 2073 K. Figure.5 shows the microscopic structure of one of the carbon aerogels synthesized.



Fig. 5. SEM image of one of the carbon aerogels synthesized (Tpyro = 2073 K) Ref(Wiener et.al, 2009)

The effective thermal conductivities of carbon aerogels according the determined values of thermal diffusivity, specific heat, and sample densities are shown for the two carbon aerogels investigated in Figure. 6. The comparison of the values derived in 0.1MPa argon atmosphere and under vacuum shows that the difference between the two datasets is almost temperature independent on the order of $0.02W \cdot m-1 \cdot K-1$. This difference in thermal conductivities represents the contribution of the gas in the pores of the aerogel to the total effective thermal conductivity.

In Figure.7, these data are compared to the experimental data of the total effective thermal conductivities measured in vacuum. The plot reveals that the radiative transport represents even at 1770K only a small contribution to the total effective thermal conductivity in the carbon aerogel investigated. The thermal transport is rather dominated by the heat transfer via the solid phase. The full line in Figure.7 corresponds to a fit of a superposition of the radiative thermal conductivity and the solid thermal conductivity the upper dashed line in Figure.7 represents the effective thermal conductivity to be expected for a carbon aerogel derived from the same organic precursor as the samples measured here, however, pyrolyzed at a temperature of 2773 K. Under 0.1MPa argon atmosphere, the values are expected to increase by an additional constant term of about 0.02W m⁻¹·K⁻¹.

It showed that the thermal conductivity via the backbone of carbon aerogels is strongly increasing with the pyrolysis or the annealing temperature applied (Wiener et.al, 2006); this is due to the increase in ordering of the carbon structure on the molecular scale accompanied by the growth of the carbonaceous microcrystallites. The study revealed that

these structural changes mainly reduce the grain boundaries and thus the scattering of the phonons dominating the heat transport via the solid phase. In contrast, the electronic contribution to the thermal transport was shown to be negligible as expected for highly amorphous systems. Nevertheless, the earlier paper already revealed the high potential of carbon aerogels as high-temperature thermal insulations.



Fig. 6. Thermal conductivity of the investigated carbon aerogel (pyrolysis temperature=2073K) as a function of temperature under 0.1MPa argon atmosphere (filled circle) and vacuum (open circle). Also shown is the thermal conductivity of a carbon aerogel (pyrolysis temperature = 1073K) at 573K in 0.1MPa argon atmosphere (filled triangle) and vacuum (open triangle). Ref(Wiener et.al,2009)



Fig. 7. Thermal conductivities of a carbon aerogel (pyrolysis temperature=2073K) measured as a function of temperature in vacuum (open circle). Radiative λ r and solid λ s contributions to the thermal conductivity are indicated; full line represents the superposition of the two terms. Upper dashed line corresponds to the thermal conductivity expected for the same aerogel, however, pyrolyzed at 2773K. Ref(Wiener et.al,2009)

2.3 Production of SiO₂-based aerogels with opacifier addition

Pure Aerogel is poor thermal insulator because it is highly transparent in the special wavelength regions (i.e., from 3 to 8μ m). To improve its thermal insulation capacity, approaches such as doping aerogel with TiO₂, K₂Ti₆O₁₃ whisker or carbon black could minimize the infrared radiation heat transfer. The opacifier has the ability to suppress radiation transport by eliminating the infrared transparent window of aerogel.

In our previous studies, SiO_2 composite aergoels-doped $K_2Ti_6O_{13}$ whisker (2–8 wt.% $K_2Ti_6O_{13}$ in the final aerogel) were prepared according to the acid (HCl)-catalyzed sol-gel procedure. Briefly, tetraethoxysilane (Si(OC₂H₅)₄, Aldrich 98.5%, TEOS), EtOH, HCl and H₂O with molar rations of 1:7:4 were used as precursors for the silica. The pH value of above mixture was adjusted to 2 by HCl (0.2 mol/L).

The $K_2Ti_6O_{13}$ whisker (diameter of 1–2µm and length of 10–50µm, 95% purity) was ultrasonically dispersed for 60 min in the TEOS/EtOH/H2O mixture. Then the mixturedoped $K_2Ti_6O_{13}$ whisker was refluxed at 80 °C for 40 min, followed by the addition of 0.25 ml of 0.05 mol NH₃ H₂O and mixed for about 10 min until the transparency appear. After 24 h of aging in TEOS/EtOH solution to strengthen the gel network structure, the pore fluids in wet gel were exchanged with ethanol by turns to facilitate following surface modification. Subsequent modification was preceded by immersing wet gel in cyclohexane solution at 30°C for 48 h. Modified wet gel was dried in the oven at 65°C for several days and further heat-treated at increasing temperature up to 500, 700, 800, 900 and 1000°C for 2 h. In this study, the aerogel before the heat-treatment is designated as the "as-dried aerogel." The mass percentage of $K_2Ti_6O_{13}$ whisker in total silica-based aerogels was 2% for KT-2, 4% for KT-4, 6% for KT-6, and 8% for KT-8.

As for TiO₂ additive, firstly SiO₂–TiO₂ gels were prepared with the acid (HCl)-catalyzed solgel method by using tetraethoxysilane (TEOS) as precursors, which follows the same trend of chemical reactions of aeogels doped $K_2Ti_6O_{13}$ whisker. The TiO₂ (TiO₂ KA-100, rutile crystalline phase, mean particle size = 50 nm) nano-powder were firstly ultrasonically dispersed for 60 min in the TEOS/EtOH/HCl/H₂O mixture. The content of TiO₂ powder is 1, 3, 5 and 10 wt.%, respectively. The detailed processing for preparing aerogels with opacifier addition is listed in Figure.8

3. Microstructure

3.1 Microstructural and structural feature for SiO₂-TiO₂ system

Figure.9 shows the microstructure of silica matrix aerogel composite observed by SEM. TiO_2 particles were dispersed within silica aerogel matrices and most TiO_2 particles were adhered to silica network. As the arrows in Figure.9 indicated, there are small irregularly localized white particles with uniform diameters of approximately 50 nm. These nanoparticles are attributed by EDS analysis (not shown here) to titania oxide (TiO_2) incorporated into silica glass.

TEM micrographs of the obtained aerogels are also presented in Figure.10(a) and (b). It can be observed that silica aerogels exhibit a sponge-like microstructure. The spherical SiO₂ particles with a size of a few tens of nm form a 3-dimensional network containing homogeneous pores (size in the range of 10–15 nm). The HRTEM image, also shown in Figure.10(c), indicates that the spherical TiO₂ particle is embedded into amorphous silica and the interface between silica aerogel and TiO₂ is clean.







Fig. 9. SiO₂ aerogels doped with different TiO₂ content (a) 1 wt.%; (b) 3 wt.%; (c) 5 wt.%; (d) 8 wt.%.



Fig. 10. TEM and HREM of prepared aerogel for ST5 (a) TEM of nano-porous silica aerogel; (b) TiO_2 particle incorporated in silica aerogel; (c) HREM for interface between silica aerogel and TiO_2 particle.

Figure. 11 shows the XRD patterns from ST5 heat-treated ranged from 500 to 1000°C. It could be seen that the presence of amorphous silica appeared as a large band cantered at 21°. The crystal peaks were found during the whole temperature ranges due to the addition of TiO₂ and all of the TiO₂ peaks are rutile phase. FTIR spectra of the prepared silica aerogel and ST5 heat-treated at different temperature are indicated in Figure.12 and 13, respectively. The peaks at 3400 and 1644 cm⁻¹ correspond to the O–H absorption band, which is caused by physically adsorbed water. The peaks near 460, 800, and 1091 cm⁻¹ are due to Si–O–Si bending modes, symmetric Si–O–Si stretching vibration and asymmetric Si–O–Si stretching vibration, respectively. Additionally, the bands at 2920 and 1400 cm⁻¹ were assigned to C–H vibrations. The latter C–H could be attributed to organic residues, which remained in prepared aerogels even after calcinations.



Fig. 11. XRD patterns of ST5 according to various heat-treatment temperature.



Fig. 12. FTIR spectra of composite silica aerogels according to various TiO_2 additives.



Fig. 13. FTIR spectra of ST5 heat treated at different temperature.



Fig. 14. Pore radius distribution of SiO2 aerogels with different TiO2 content

The peak of pore size distribution increased with the more TiO_2 additive (see Figure.14). It is observed that for all the samples the pore size distribution curves are in the range 10–60 nm with a relative narrow pore distribution centred around 30–45 nm. The pore diameter of ST1 was the minimum. Then as the TiO_2 content increased, the pore diameter increased slightly. It is known that aerogels are mainly comprised of mesopores below 50 nm. Considering the maxim pore size had exceeded 2µm by nitrogen absorption and desorption method (Table.2), silica composite aerogel could have macropores larger than 2µm. The fact is supported by smaller pore volume and specific surface area for ST10.

Sample	Pore volume	d_{\max}	Specific surface	d_{average}
	(cm^{3}/g)	(nm)	$area(m^2/g)$	(nm)
1%TiO ₂	1.219	318.53	1210	30.28
3%TiO ₂	0.985	2999.3	1026	38.42
5%TiO ₂	1.040	3398.8	1089	38.20
10%TiO ₂	0.898	2235.3	785	45.73

Table 2. Properties of SiO₂-TiO₂ aerogels obtained via ambient pressure dying

Figure 15 shows the nitrogen adsorption-desorption isotherm of silica doped TiO₂ aerogels. The ST1, ST3 and ST5 samples exhibit typical type-IV adsorption isotherms, which are considered to indicate the presence of mesopores. There are shifts in the loops, but the basic shape seems to be constant. All the adsorption of N2 increases first, and then decreases with a maximum at ST1 due to more capillary condensation in the mesopores, which gives the larger surface area. Compared with the ST1, ST3 and ST5, the ST10 aerogels exhibit type-II adsorption isotherms and the ST10 sample has low adsorption and almost no hysteresis. Because higher TiO₂ content may lead to the TiO₂ agglomeration during sol-gel process, and these agglomeration will close some mesopores and cause the breakage between the SiO_2 and TiO_2 interface in local area, which is reflected in the lower surface area and lower pore volume. Generally the SiO₂ aerogel possesses the potential to form a highly porous structure, giving large surface area and pore volume. While mixing TiO_2 into SiO_2 aerogel, the textural properties of the composite aerogels may change due to the interaction between them. The specific surface area of the aerogels slightly decreased, from 1210m2/g for the ST1 to about 785m²/g for ST10. The pore volume of the composite aerogels changes slowly, decreasing from $1.219 \text{ cm}^3/\text{g}$ for ST1 to $0.898 \text{ cm}^3/\text{g}$ for ST10. The decreasing of the pore volume is due



Fig. 15. BET of SiO₂ aerogels with different TiO₂ content

to the enhancement of the pore size in both the micropore and mesopore ranges due to the incorporation of TiO_2 into the framework of SiO_2 .

3.2 Microstructural and structural feature of SiO₂-K₂Ti₆O₁₃ whisker composite aeogels

Figure.16 shows the microstructure of silica matrix aerogels composite observed by SEM. $K_2Ti_6O_{13}$ whisker were dispersed within silica aerogel matrices and most $K_2Ti_6O_{13}$ whisker were adhered to silica aerogels. When silica aerogel parts were magnified, 10–20nm sized pores and 10–30nmsized spherical solid clusters were known to be existed. TEM micrographs of the obtained aerogels are also presented in Figure.17. It can be observed that silica aerogels exhibit a sponge-like microstructure. The spherical SiO₂ particles with a size of a few tens of nanometers form a three-dimensional network containing homogeneous pores (size in the range of 10–15 nm).

Figure.18 shows the XRD patterns for KT-6 heat-treated at different temperatures. It could be seen that the aerogels were amorphous below 800°C and only some negligible K2Ti6O13 crystal peaks were found around 25.4°. However, XRD patterns show halo in the range of 20–22° corresponded to the characteristic peaks of silica crystalline and $K_2Ti_6O_{13}$ up to 900°C. It can be concluded that the phase transformation for silica aerogel might occur from amorphous phase to crystalline state above 800°C.



Fig. 16. SEM photographs of silica aerogel composite (left) and magnified silica aerogel part (right).



Fig. 17. TEM image of silica aerogel parts in SiO₂- K₂Ti₆O₁₃ system



Fig. 18. XRD patterns of KT-6 according to various heat-treatment temperatures

FTIR spectra of the prepared silica aerogel are indicated in Figure.19. The peaks at 3438 and 1630 cm^{-1} correspond to the O–H absorption band, which is caused by physically adsorbed water. The absorption peaks near 1091 and 460 cm–1 are due to Si–O–Si vibrations, which will appear in any silica products. It is obvious that apart from Si–O–Si and O–H absorption peaks, the absorption peaks at 1395 and 825 cm^{-1} correspond to Si–C bonding. The spectrum shows almost the same patterns, irrespective of the additive of $K_2 \text{Ti}_6 \text{O}_{13}$ whisker. Even though the aerogels are chemically identical, there are differences in their physical properties, such as their transmittance, density and thermal stability.



Fig. 19. FT-IR spectra of composite silica aerogels according to various $K_2Ti_6O_{13}$ whisker additive (a) KT2; (b) KT4; (c) KT6; and (d) KT8.

4. Thermal properties of SiO₂-based aerogels

As the investigations described here are mainly performed in order to develop new thermal insulation materials for application at higher temperatures (mainly between 25 and 800°C), the aerogels were characterized with respect to their infrared transmittance in the wavelength range from 2.5 to $12\mu m$. For larger wavelengths (>10 μm) the transmittance of the SiO₂ skeleton is in the range of \sim 65% (Figure. 20) and thus dominates the transmittance spectrum. As is evident in Figure.20, the infrared spectra of all of the samples demonstrate that with decreasing $K_2Ti_6O_{13}$ additive there is a decrease in transmittance. This is caused by the increase in the scattering intensity according to the Rayleigh relation. For all different contents of K₂Ti₆O₁₃ additive, the transmittances of the aerogels increased slowly with increasing wavelength ranging from 2 to 7µm. The transmittance of the prepared aerogel for KT-2 was about 50% at awavelength in the range of $4-7\mu m$, while it was only 15% for the aerogel for KT-8. This difference seems to emanate from variations in the microstructure, such as the morphological change of the pores in the aerogel network structure. For a given density of silica, the microstructure, especially the secondary particle (cluster) content and size, play an important role in determining the transmittance of the silica aerogel(zhang et.al, 2009).On the other hand, most infrared wavelengths were blocked by the aerogels, regardless of the additive of $K_2Ti_6O_{13}$ whisker, so that over 55-85% of the waves were interrupted at a wavelength of around 5-7µm.

Previous studies (Wang et.al,1995) showed that the additive of TiO_2 led to a strong increase of the specific extinction and thus decrease of the radiative thermal conductivity at high temperature. $K_2Ti_6O_{13}$ whisker has a high-reflection index and negative temperature thermal conductivity (i.e., exhibiting a thermal conductivity of 0.089 and 0.017W/mK at 30 and 800°C, respectively) [Wang et.al,2005]. Thus more absorbing energy could be blocked, thereby resulting in a decrease in the transmittance with the increasing of additive of $K_2Ti_6O_{13}$ whisker.

Figure.21 shows the transmittance variation for the composite aerogels at different temperatures. It can be seen that the transmittance also changed according to the different

additives of $K_2Ti_6O_{13}$ whisker. The composite aerogels heated to temperatures at 300°C showed a transmittance of about ~35% for the near 3µm wavelength, whereas those heat-treated at more than 400°C blocked over 95% of the near the same waves. As is evident in Figure.21, the transmittance gradually decreased as the heat-treatment temperature was increased up to 600°C. According to the FT-IR and TG/DTA results, the hydrophobic surface groups disappeared and the aerogel became hydrophilic at temperatures above 320°C. Thus, the adsorption and desorption of the hydrophobic functional groups seems to be responsible for the optical behavior of the aerogels.



Fig. 20. Transmittance of the composite silica aerogels in the infrared light region. The aerogels were prepared with different $K_2Ti_6O_{13}$ whisker additive (a) KT8; (b) KT6; (c) KT4; and (d) KT2.



Fig. 21. Transmittance of the composite silica aerogels with KT6 additive heated at different temperatures (a) 100°C; (b) 350°C; (c) 500°C; and (d) 600°C.

 TiO_2 is another important opacifier to increase the thermal property for aerogels. As is evident in Figure.22, the infrared spectra of all of the samples demonstrate that with TiO_2 additive there is a decrease in transmittance. The optical properties measured here show that the transmittance of the pure SiO_2 aerogel is relative high (about 60%) on the whole range of wavelengths. The transmittance of the prepared aerogel for ST1 was near to 50% at a wavelength in the range of $3-8\mu m$, while it was below 40% for the aerogel for ST5 and ST8. Figure.23 shows the transmittance variation for pure silica aerogel and ST5 at 500°C. It can be seen that the pure aerogel even remains a high optical transmittance (exceeding 60%). Meanwhile the transmittance for ST5 was comparably decreased, especially ranging from 5 to 8µm (i.e., far below 30%). It is clear that additive of TiO₂ can greatly decrease the transmittance in room temperature as well as in high temperature. Previous reported literature also showed that the effective specific extinction increased with the amount of TiO_2 (Zhang et.al, 2010), and thus the radiative thermal conductivity or the infrared transmittance is certainly reduced, which can also be described by Rayleigh scattering theory. Usually the resulted silica aerogels are transparent, and this is because the aerogel microstructure has a small scale compared to the wavelength of light. Their transparency plays an important role in high energy physics with charged particles, while their optical transparency should be reduced for thermal insulation application.



Fig. 22. Transmittance of silica aerogels prepared with different TiO₂ opacifier

From above experimental analysis and discussion, it can be seen that transmittance of the prepared aerogels strongly depend on the opacifier content as well as the spectral wavelength. By contrast, the pure aerogels exhibits radiative properties which are remarkably stable, remaining high transmittance in the range of investigated wavelengths. Such a feature is characteristic of so-called transparent materials. Given its relatively higher transmittance, aerogel doped with TiO_2 or $K_2Ti_6O_{13}$ opacifier is a semi-transparent material with a low transmittance.

The value of thermal conductivity of SiO₂-based aerogels is listed in Table.3. For $K_2Ti_6O_{13}$ whisker addition, the total thermal conductivity decreased gradually with the increasing of $K_2Ti_6O_{13}$ whisker, which is due to the very low thermal conductivity of $K_2Ti_6O_{13}$ whisker.



Fig. 23. Transmittance of silica aerogels and ST5 at 500°C

While for TiO_2 addition, the thermal conductivity increased with the more content of TiO_2 addition. Because TiO_2 could increase the total thermal conductivity at room temperature, however, this is might be reverse at higher temperature.

Sample	Bulk density (gcm ⁻³)	Pore size (nm)	Thermal conductivity (Wm ⁻¹ K ⁻¹)
SiO ₂ aerogels	1250	26.3	0.060
KT2	843	27.6	0.057
KT4	741	27.9	0.055
KT6	688	27.7	0.054
KT8	694	29.5	0.051
ST1	1210	30.28	0.061
ST3	1026	38.42	0.063
ST5	1089	38.20	0.065
ST10	785	45.73	0.072

Table 3. Thermal conductivity of SiO₂-based aeorgels

5. Summary and future perspectives

Aerogels have a wide variety of exceptional properties, hence a striking number of applications have developed for them. Many of the commercial applications of aerogels such as catalysts, thermal insulation, windows, and particle detectors are under development and new applications have been developed, but little in the way of actual use has resulted (Soleimani Dorcheh & Abbasi,2008;). However, monolithic silica aerogel has been used extensively in high energy physics in Cherenkov radiation detectors. Other application of silica aerogels are: shock wave studies at high pressures, inertial confinement fusion (ICF), radioluminescent devices and micrometeorites (Barbieri et.al, 2001; Beck et.al, 1989;Bhagat, et.al, 2006; Bhagat, et.al, 2007;Bisson, et al, 2004).

Property	Features	Application
Thermal conductivity	 Best insulating solid Transparent High temperature Lightweight 	 Architectural and appliance insulation, transport vehicles, pipes Space vehicles and probes, casting molds
Density /porosity	 Lightest synthetic solid Homogeneous High specific surface area 	 Catalysts, sorbers, sensors fuel storage, ion exchange Targets for ICF, X-ray lasers
Optical	 Low refractive index solid Transparent Multiple compositions 	Cherenkov detectors, lightweight optics, lightguides, special effect optics
Acoustic	• Lowest sound speed	Impedance matchers for transducers, range finders, speaker
Electrical	 Lowest dielectric constant High dielectric strength High surface area 	 Dielectrics for ICs, spacers for vacuum electrodes, vacuum display spacers, capacitors

Table 4. Property, features and application of aerogels

It is interesting to compare the various exceptional properties and features of aerogels with their real or prospective applications. This gives an idea of the tremendous variety of aerogel applications and hints at the impact that these materials will have as we view their future uses. Table 3 lists some possible applications, both general and specific, which result from particular properties of the aerogels.

Although there are many challenging problems to be solved before the application of aerogels, it has verified that aerogels as a class of materials, have already demonstrated an incredible versatility of applications; probably having no comparable competitor in recent years. It can be said that the full impact of these materials for public use is yet to come. It is doubtful that it will happen until the cost of producing these materials is reduced and the price becomes competitive with other polymer materials. While this may still be a few years away, the authors believe that the common use and availability of aerogels is inevitable.

6. Conclusion

This chapter provides a comprehensive introduction of the synthesis, structure, thermal properties and characterization of silica aeorgels. Aerogels show great promise for use in variety of technological areas where special structure and physical properties are required. Substantial progress has been made in the development, processing and characterization of areogel materials over the recent years. Special attention has been paid to the use of inexpensive precursors and the drying technology to make the production commercial.
Silica aerogel synthesis with various materials and process conditions and also the properties and method determination are reviewed and supplied in this chapter.

7. References

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Polymer Nanocomposite Materials for Structural Applications

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1. Introduction

The improvements of physicochemical and thermomechanical properties of polymer composite materials has been a major research interest in the last few decades. Polymer nanocomposites (Mohammad, 2006; Xiangling, 2003) represent a new class of materials alternative to conventional filled polymers. In this new class of material, nanosized inorganic filler (at least one dimension) are dispersed in polymer matrix offering tremendous improvement in performance properties of the polymer. Nanoscale materials have been the subject of research interest in recent years because of their unique properties as compared to the bulk counterparts and their potential applications in a wide variety of areas such as information storage, electronics, sensors, structural components, and catalysis etc. The main challenge challenge in fabrication of these polymer nanocomposites for structural applications is uniform dispersion of nanoparticles in the polymer matrix. However, good dispersion for nanoparticles in polymer composite materials is extremely difficult to achieve, since nanoparticles tend to aggregate together during fabrication. The degree with which the nanoparticles can be homogeneously dispersed in the polymer matrix would significantly influence the thermal, mechanical and optoelectronic properties of the material. Researchers have used several techniques for dispersing nanoparticles may include: 1) mechanical agitation, such as ball milling or magnetic stirring, 2) ultrasonic vibration, 3) shear mixing 4) non-contact mixing 5) using the dispersing agent. The process of curing of these polymer is an another important factor in improving the mechanical, thermal, electrical and optical properties. There is an ever-increasing demand for development of processing of polymer nanocomposites for advanced structural applications. In polymer composite fabrication, curing (polymerization) step is crucial and time-consuming process. The processing thermoplastic nanocomposites were carried out using melt extrusion, or solution casting. The epoxy based thermoset polymers are generally cured using conventional heating. The manufacturing industries of these nanocomposites are also in need of quick and efficient curing method for high temperature or room temperature curing of epoxy polymers. The conventional method of curing is timeconsuming, the longer it takes to complete a project, the more expensive it becomes. Several alternate curing methods have been tested and they are: UV rays, Gamma rays, Electron Beam and Microwave (Bogdal & Karen, 2003; Clark & Sutton, 1996), microwave heating curing of room or high temperature epoxy resins. The current chapter is focused on fabrication techniques, synthesis, and characterization of four main polymeric

nanomaterials for various applications: a) Dispersion, synthesis, and curing of epoxy-based nanocomposites, b) Polymeric foam core nanocomposites for lightweight and high strength applications c) Alignment of acicular nanoparticles in thermoplastic polymers to improve the mechanical and antimicrobial properties of textile fibers. d) Development of shear thickening fluid for liquid body armor applications.

2. The dispersion, synthesis, and curing of epoxy-based nanocomposites

The epoxy based nanocoposites are generally prepared by dispersion of known amount of nanoparticles in one of the non-reactive parts of the resin and mix with reactive part of the resin and finally cure. Depending on the physical and chemical properties of nanoparticles, and epoxy resin the processing technique is selected. Most of the commerical metal, metal oxide, and carbon based nanoparticles are used as received. Where as some of the high density and highly agglomerated/entalgled nanoparticles such as WO₃ and CNTs require a special modification for better dispersion to obtain optimal improved properties. In one of our recent studies a high density WO₃ anopaticles were subjected to sized reduction process for better dispersion and improve mechanical properties. The porous WO₃ (pore size 2-5nm) nanoparticles were synthesized using a high intensity ultrasound irradiation of commercially available WO₃ nanoparticles (80nm) in ethanol. The nanocomposites of WO₃/ SC-15 epoxy were prepared by infusion of 1wt%, 2wt% and 3wt% of porous WO₃ nanoparticles into SC-15 epoxy resin by using a non contact (Thinky) mixing technique. In this technique the material container is set at 45 degrees angle inside the mixer and revolves and rotates at high acceleration with the speed of ~ 2000 rpm, dual centrifugal forces were given to the container that keep pressing materials to outward and down along with the slope of inner wall of the container and accomplish powerful mixing and removing air pockets formed in the reaction mixture simultaneously. This technique is non contact and non reactive unlike ultrasound and other mixing techniques (Guo et al., 2006; Isobe et al., 2006; Allaoui et al., 2008; Rao et al., 2003). The mixture was degassed using a vacuum oven for 30 minutes and the finally the neat epoxy and nanocomposites were cured at room temperature for about 24 hours in a plastic rectangular mold. The known percentages of the WO₃ nanoparticles were dispersed in epoxy part-A (SC-15, applied polyramics) using a noncontact defoaming mixer (Thinky, Japan) for 15 minutes. The part-B of the resin was then added to the mixture of part-A containing WO₃ and mixed again using a noncontact defoaming mixer for another 10 minutes. Finally the resin mixture was poured into a polypropylene container and cured at room temperature for 24 hours. This procedure was repeated for three different weight percentages of the WO₃ nanoparticles (1wt%, 2wt% and 3wt %) to make the epoxy nanocomposite and neat epoxy. The samples were cut precisely and used for the microscopic and mechanical testing.

Figure 1(a) shows the TEM picture of the as-received WO₃ nanoparticles. The particles are nearly spherical in shape and the size distribution is wide (\sim 30-100nm). The high resolution micrograph (shown in Figure 1(a)) clearly shows that there are no pores in the as received WO₃ nanoparticles where as the Figure 1(b) clearly shows that the sonochemically modified WO₃ nanoparticles are porous and typical pore size is \sim 2-5 nm. These TEM results indicate that without significant change in the particles sizes the pores are created uniformly all over the particles using high intensity ultrasound irradiation. SEM micrographs of dispersion of as-received WO₃ nanoparticles and sonochemically modified WO₃ nanoparticles are shown in Figure 1(c) and (d) respectively. It is noteworthy to mention that the infusion of asreceived WO_3 in epoxy resulted in clear separation of particles and epoxy as seen in Figure 1(c). This indicates that the particles are high in density and they are not compatible with the epoxy resin. Whereas the infusion of sonochemically modified WO_3 nanoparticles resulted in uniform dispersion of nanoparticles over the entire volume of epoxy resin presented in Figure 1(d). To study the real effect of dispersion on mechanical properties we have carried out the compressive behaviour of $WO_3/SC-15$ epoxy nanocomposites.



Fig. 1. TEM micrograph of a) as-received WO₃ nanoparticles, b) sonochemically modified WO₃ nanoparticles, c) SEM images of as-received 1wt% WO₃ nanophased SC-15 epoxy nanocomposite and (d) and (e) SEM and TEM micrographs of sonochemically modified 1wt% WO₃ nanophased SC-15 epoxy nanocomposite respectively.



Fig. 2. Compressive stress-strain curves of neat and nanophased SC-15 epoxy nanocomposites

The quasistatic compression tests were carried for neat and nanocomposite samples. Stressstrain curves of 1wt% 2wt% and 3wt% of WO₃/SC-15 epoxy along with neat SC-15 epoxy are shown in Figure 2. It is observed from Figure 2 that the compressive strength and modulus of the 1wt% WO₃/SC-15 epoxy system is 92 MPa and 1773 MPa respectively. Whereas the neat SC-15 epoxy compressive strength and modulus are 79MPa and 894MPa respectively. These results shows that the 16% increase in strength and 98% increase in modulus as compared to the neat SC-15 epoxy system. The 1wt% loading of WO3 nanoparticles shows the highest mechanical properties among the 2wt% and 3wt% loading of WO₃ nanoparticles. The higher (2wt% and 3wt%) percentage loading of WO₃ nanoparticles shows the inferior properties compared to the 1wt% loading of WO₃ nanoparticles but still they are higher than the neat SC-15 epoxy polymer. The reason for this may be explained as particle loading increases the resulting composites will begin to see more and more particle-to-particle interaction rather than the intended particle-to-polymer interaction. Particle to- particle interaction will lead to agglomerated particles and poor mechanical properties. These mechanical properties are consistence with the thermal and microscopic properties. Figure 2 also contain a stress plateau region that indicates that these composites have an ability to absorb compressive damage. These curves are similar to those observed by other researchers (Gupta & Ricci, 2006).

Because of the wide spread applications of polymer nanocomposites they have created a new opportunity for the development of high performance, smart and multifunctional nanocomposites materials. Recently nanocomposites have shown significant improvements in their mechanical properties. However the advancement of synthetic methods for developing new types of nanofillers in the last two decades has sparked an opportunity for the development of multifunctional nanocomposite materials. A single material with more than two functionalities such as improved mechanical properties along with magnetic, electrical optical, and sensing capabilities. It is also know in the literature that the decoration of CNTs with metal or metal oxides can improve dispersion of CNTs in solvents (Oh-Kil et al., 2003; Chin et al., 2004; Oymak et al., 2004; Watts et al., 2002; Wu et al., 2002) or reveal new

optical, electric, manetic properties of CNTs (Lidström et al, 2001; Alexandre et al., 2000; Wiesbrock et al., 2004; Kerep et al., 2006). To address some of the multifunctionalities of a materials we have prepared the iron oxide nanoparticled coated on CNTs. These nanoparticles were further used to fabricate $Fe_3O_4/CNTs$ epoxy nanocomposite and tested for their mechanical and microscopic properties. Prior to curing, the epoxy resin was mixed with known weight percentages of CNTs (0.5 wt% and 1 wt %) using a non-contact (Thinky hybrid defoaming mixer ARE-250) mixing for 10 minutes. A stoichiometric amount (26 wt %) of the curing agent (epicure W) was added to the reaction mixture containing epoxy and CNTs or $Fe_3O_4/CNTs$ and mixed for another 10 minutes. The mixture was degassed using a vacuum oven for 30 minutes and the final reaction mixture was transferred into a stainless steel mold for curing. The epoxy resin with and without CNTs or Fe_3O_4 nanoparticles were cured at 120°C for 2 hours and post-cured for 2 hours at 150° C in an oven. The as-fabricated nanocomposte is tested for dispersion and mechanical properties.



Fig. 3. TEM micrographs of (a) pristine CNTs dispersion in Epon-828, (b) Fe_3O_4 nanoparticles coated on CNTs dispersion in Epon-828, and (c) EDS micrograph showing Fe_3O_4 nanoparticle on CNTs in Epon-828 epoxy

TEM studies were carried out to study the dispersion of CNTs and $Fe_3O_4/CNTs$ in the Epon-828 resin. The TEM micrographs of nanocomposite samples of a) 0.5wt% CNTs/Epon-828 and b) 0.5wt% $Fe_3O_4/MWCNTs/Epon-828$ are presented in Figure 3(a) Figure 3(b) respectively. Figure 3(a) shows that the CNTs are well dispersed in the Epon-828 resin. As

seen in micrograph (Figure 3(a)) the CNTs are completely covered with resin and particles. They are well dispersed in the Epon-828 resin as compared to the pristine CNTs (Figure 3(a)). The dispersion of Fe₃O₄ coated CNTs in Epon-828 resin is shown in Figure 1(b). This Figure clearly shows that the Fe₃O₄ coated CNTs are well dispersed over the entire volume of the Epon-828 resin with a no agglomeration. In this micrograph we can also see that the Fe₃O₄ nanoparticles adhere on the CNTs after dispersion in the Epon-828 resin. This clearly shows that the noncontact mixing method is efficient in mixing the coated nanoparticles in Epon-828 resin. To confirm the coating of Fe₃O₄ nanoparticles on CNTs the EDS analysis was carried out and the results are presented in Figure 3(c). These results show the presence of Fe, O and C elements at nanoscale. The Cu peaks are assigned to the copper grid.

To study the effect of coating of CNTs on mechanical properties, flexural properties of the Fe₃O₄/CNTs- Epon-828 epoxy were measured. Flexural specimens were prepared according to ASTM standard D790-01. The specimens were tested using Zwick/Roell Material Testing Machine. The load cell used on the Zwick/Roell machine is approximately 2.5 kN. The test was carried out in displacement control mode and the cross-head speed was 2 mm/min. TestXpert software was used to analyze the load-deflection data recorded by the data acquisition system. A Flexure test produces a tensile stress in the convex side of the specimen and compression stress in the concave side. This creates an area of shear stress along the midline. Flexure test measures the force required to bend a specimen under 3 point loading condition. In a 3-point test the area of uniform stress is quite small and point concentrated under the center loading point The Flexural test measures were carried out under a 3 point bend loading conditions at ambient temperature.



Fig. 4. Flexural stress-stain curves of a) neat Epon-828, b) 0.5wt % of Pristine MWCNTs c) 1wt% of Pristine MWCNTs d) 0.5wt% of Fe₃O₄ coated MWCNTs/Epon-828, and e) 1wt% Fe₃O₄ coated MWCNTs/Epon-828

The stress- strain curves of the neat Epon-828 and coated CNTs and uncoated CNTs infused Epon-828 resin are shown in Figure 4. The Figure 4 shows flexural stress-stain curves of a) neat Epon-828, b) 0.5wt % of uncoated CNTs c) 1wt% of uncoated CNTs d) 0.5wt% of

magnetite coated CNTs and d) 1wt% magnetite coated CNTs. The rest results were presented in Table 1. These results show that there is a gradual increase in the flexural modulus and strength. With the addition of the pristine CNTs (1wt%) and coated CNTs(1wt%) the strength increases to 20% and 50% respectively as compared to the neat Epon-828 epoxy.

Sample	Ultimate Flexural Strength GPa	Flexural Modulus GPa
Neat Epon-828	0.078	2.19
0.5% Pristine/ CNTs/Epon-828	0.093	2.34
1% Pristine / CNTs/Epon-828	0.094	2.67
0.5% Fe ₃ O ₄ /CNTs/Epon-828	0.099	2.70
1% Fe ₃ O ₄ /CNTs/Epon-828	0.117	2.84

Table 1. Flexural properties of neat Epon-828 and nanocomposite systems

There is an ever-increasing demand for development of processing of polymer nanocomposites for advanced structural applications. The manufacturing industries of these nanocomposites are in need of quick and efficient curing method for high temperature epoxy polymer. Over the last five decades the applications of microwave radiation has been increased tremendously in various scientific research fields. The application of microwave heating in curing processes of composites are very limited because of the complexity involved in heat absorption of multiple components at different rates simultaneously. In polymer composite fabrication, curing (polymerization) step is crucial and time-consuming process. Curing can be done by either at room temperature or at high temperature but both types of curing take prolong time (one or two days) (Lidström et al, 2001). This is ultimately adds up to the final cost of the product.

Recent studies have shown that the nanocomposites exhibit remarkable improvements in stiffness, strength, physio-chemical and thermal properties without compromising on density, toughness, or processibility compared to their micro and macro composite counterparts (Alexandre, 2000). Field of polymer nanotechnology is still unrefined in certain aspects, curing is one of them. Novel techniques of curing bring out new breakthrough and there are avenues in nanotechnology, which have not been discovered yet. The bulk manufacturing and energy saving curing methods of nanocomposites is one such major unexplored research areas. The conventional method of curing is time-consuming, the longer it takes to complete a project, the more expensive it becomes. Alternate curing methods have been tried and tested for quite some time now. They are: UV rays, Gamma rays, Electron Beam and Microwave (Bogdal et al., 2003; Clark & Sutton, 1996). Curing using UV light has limited application because of its poor penetrability and limited dose rate; it cannot cure thick materials (Wiesbrock et al., 2004). Gamma rays induced radiation hazard and environmental issues. The most prominent alternatives suggested are Electron Beam (EB) and Microwave heating (Kerep & Ritter, 2006; Sinnwell & Ritter, 2006). Electron Beam curing though efficient and fast unfortunately requires high capital cost for initial setup Ghosh & Palmese, 2005). It has some other drawbacks like low glass transition temperature (or low service temperature), low fracture toughness, and high shrinkage when cured (Ghosh & Palmese, 2005). Microwave curing, therefore, is the more economically feasible alternative and is remarkably energy efficient (Soane & Martynenko, 1989; Jacob et al., 1995; Zhou & Hawley ,2003). Microwave heating is unique in the fact that heat is generated in the specimen rather than externally transferred. The potential for microwave curing stems from the fact that there are no major drawbacks for this method. The curing of nanoparticles infused epoxy using microwaves is a relatively unexplored area of research. A novel method has to be formulated from testing different conditions of cure selecting from factors such as power level of microwave, time to cure, percentage of nanoparticles infusion, method of infusion and finally relative cost than other technique. Recently (Papargyris et al., 2008) reported a 50% cure cycle time reduction through the use of microwave curing of carbon fibre epoxy composite prepared by RTM technique without loosing its mechanical and thermal properties. (Sandhya et al., 2006) also reported that the microwave curing of the glass-reinforced epoxy resin system is thirty times faster and twenty times more energyefficient as compared to the oven cured. They also reported that the mechanical performance of the microwave-cured glass-epoxy composite under tension, compression, and flexure, is in close comparison to the thermally cured glass-epoxy composite.

Recently, several studies have been conducted to investigate the interaction between microwave radiation and CNTs. (Mendez, 2003; Watts, 2003; Wu, 2004; Watts, 2003; Grimes et al., 2000; Petit et al., 1997; Imholt et al., 2003). Very recently Chin and his group (Wang et al., 2007) reported the strong bonding between CNT and polymer by microwave heating. Still more studies are required to develop optimal processing techniques to speed up microwave processing for industrial applications. A novel method has to be formulated from testing various polymer cure conditions, microwave power levels, time of exposure to complete cure, percentage of nanoparticles infusion, method of infusion and finally relative cost than other technique.

In this current study, CNTs infused in EPON 862 nanocomposites were prepared with different weight percentage of CNTs by thermal curing (TC & TPC) followed by post curing and microwave curing (MWC). compression properties were studied. The CNTs were dispersed through acoustic cavitations process. Part-A of EPON 862 was selected for infusion of CNTs because of its less reactivity to ultrasonic irradiation. Pre-calculated amount of CNTs and part A were carefully weighed and mixed together in a beaker. The reaction mixture was irradiated with ultrasonic horn (Ti-horn, 20 kHz, 100W/cm²) at 50% of amplitude for 15 minutes. In order to avoid a temperature increase during the sonication process, external cooling was employed by submerging the mixing beaker in a thermostatic bath at 10°C for the entire period of the ultrasonic irradiation. The Part B was mixed with modified Part A using a THINKY hybrid de-foaming mixture ARE-250 at 2000 rpm for 15 minutes. The trapped air and initial reaction volatiles were removed from the mixture by using a vacuum desiccator. Finally the mixture is cured using a 2.45GHz (Microwave Processing Oven BP210) microwave oven for only 10 minutes instead of 8 hours of conventional oven heating (curing cycle is 4 hrs @ 120°C and post curing @ 170 °C for 4hrs). Same manufacturing procedure was followed for fabrication of neat EPON 862 epoxy sample without CNTs. Thermal and mechanical tests were performed for all samples including thermally and microwave cured samples.

Compression test is carried out to measure the load carrying capacity of a material before fracture. It can be seen in Figure 5 that stress-strain curves have two major distinct phases – an initial elastic response and a protracted plateau. The elastic region is controlled by the

stretching of the EPON-862 polymer. The stress plateau is associated with the time taken to form matrix cracking and crack propagation followed by barreling/bulging and increase in the lateral dimension of the rectangular samples.



Fig. 5. Compression stress-strain graphs of microwave cured (a) neat EPON-862 (b) EPON-862+0.1wt% CNTs c) EPON-862+0.2wt% CNTs d) EPON-862+0.3wt% CNTs.

Figure 5 is the compression graphs of microwave cured neat EPON 862 and EPON 862 with 0.1wt%, 0.2wt%, and 0.3wt% of CNTs loading. The compression strength/modulus calculated from the graph are: 114.44 MPa/2.24 GPa, 118.97 MPa/2.40 GPa, 120.29 MPa/2.52GPa and 118.92 MPa/2.32 GPa for neat EPON 862, EPON 862/0.1wt% CNTs, EPON 862/0.2wt% CNTs, and EPON 862/0.3wt% CNTs respectively. These results show that the 0.2wt% of CNTs infusion in EPON-862 compression modulus (28.57%) and compression strength (5.57%) increased with respect to neat EPON-862 TC and TPC. These results also summerized in table 2 for comparison. The reason for the increase in strength and modulus is may be due to the welding mechanism (Wang et al., 2007). Which is thought to involve the wetting of the CNTs by the surrounding polymer melt; a nanometer-sized melted polymer region is likely formed around the nanotubes due to the dissipation of heat from the CNTs to polymer. This local melting leads to physical intercalation of the CNTs and the polymers and yielding a bonding strength two order of magnitude higher than that obtained for polymer bonded together by epoxy adhesive.

3. Polymeric foam core nanocomposites for lightweight and high strength applications

Polymeric foam materials are widely used in many industrial applications for their properties of light weight, excellent strength to weight ratio, superior insulating abilities, energy-absorbing properties, low thermal conductivity, high sound absorption, and large compressive strains. The main applications include sandwich structures, airframes, transportation vehicles, boat hulls, radar systems, and space structures (DIAB Inc, 2002; Rohm, 2002; Baltek Corp, 2002; Marsh, 2002). High-performance structural foam materials are fabricated using a blowing agent (surfactants, hydrocarbons) in liquid polymers to expand and form rigid, low-density foams. Some of the leading thermoplastic foams made in this way are polymethacrylimide (PMI) and partly cross-linked polyvinyl chloride (PVC), with trade names Rohacell Rohm, 2002, Divinycell DIAB Inc, 2002; and Expancel Expancel®, 1980). Hollow thermoplastic microspheres are produced under the trade name of Expancel®. These microspheres are small, spherical plastic particles consisting of a polymer shell encapsulating a hydrocarbon gas. When the gas inside the shell is heated, its pressure increases and the thermoplastic shell soften, resulting in a dramatic increase in the volume of the microspheres (Elfving & Soderberg., 1994). Researchers are using these microspheres for various applications such as car protection, corrosion resistance, acoustic insulation, body fillers and marine hobby putties, underbody coatings and synthetic wood Expancel (Expancel®, 1980; Tomalino & Bianchini, 1997). Young-Wook and his coworkers (Kim et al., 2004) developed a closed-cell silicon oxycarbide foams with cell densities greater than 109 cells/cm³ and cells smaller than 30 μ m were obtained from a preceramic polymer using expandable microspheres. (Vaikhanski et al., 2004) were also studied the reinforcement of microspheres in PVC with the aramid fibers and reported the improved mechanical properties.

Expancel-092-DU-120 is unexpanded thermoplastic polymeric powder (particles sizes 28-38µm) was received from Expancel Inc. Multi walled carbon nanotubes (CNTs-10-20nm in diameter and 0.5-20µm in length) were purchased from Nanostructured & Amorphous materials. The experimental procedure for the coating of CNTs on thermoplastic microspheres and the fabrication of CNTs/thermoplastic microspheres foam panels are as follows: Expancel polymeric powder and a known weight percentage of CNT were dispersed in n-hexane using a high intensity ultrasonic horn (Ti-horn, 20 kHz, and 100 W/cm²) at room temperature for 1-hour. The mixture was then dried in a vacuum for 12hours and remaining n-hexane was removed by heating the sample at 60°C for 1-hour. The dry CNTs/thermoplastic microspheres mixture was transferred to a rectangular aluminum mold (4''X 4''X1/2'') and uniformly spread over the entire volume of the mold. The mold was then heated to ~190°C at a heating rate of 10° C/min for 30 min under a pressure of 15 atm using a MTP-14 programmable compression molding equipment. The as-prepared samples were cut precisely and used for morphological thermal and mechanical testing. The densities of as-prepared foam samples of CNTs / microspheres (nanocomposite) and thermoplastic microspheres only (neat) were measured and presented in Table 2. The as prepared foam samples without CNT are ~ 154 Kg/m^3 and with CNT are ~ 153Kg/m^3 . The smaller variations in densities of nanocomposite and neat foam samples are due to the density differences in as-received microspheres and CNTs.

To examine this we have carried out the SEM analysis at higher magnification as shown in Figure. 6. These results show that the CNT are uniformly coated on the expanded microspheres. This uniform coating with adhering of the MWCNT on microsphere translated in to the enhanced compression strength and modulus. Compression tests were carried for neat and nanocomposite foams. Nanocomposite (1% and 2 by wt %) and neat were tested. Stress-strain curves for neat and nanocomposites are shown in Figure. 7. It is observed that the compressive stress of the 2 wt% nano system is about 51 wt% higher than the neat sample. The 2 wt% nano system also shows 40 wt% improvements in compressive

modulus. This improvement may be the result of increasing the interfacial bond between the nanoparticles and polymeric matrix.



Fig. 6. Coating of CNTs on Expancel microspheres



Fig. 7. Compressive stress-strain curves are neat, 1% CNT and 2% CNT nanocomposite foam

Expancel polymeric powder and the 1wt% of SiC or SiO₂ (1wt% of SiC or SiO₂ and 99wt% expancel power) was dispersed in n-hexane using a high intensity ultrasonic horn (Ti-horn, 20 kHz, 100 W/cm²) at room temperature for 1hour. The mixture was then dried in a vacuum for 12hrs and excess n-hexane was completely removed by heating the sample to 60°C for 1-hour. Nanocomposite foam panels were fabricated by heating the dry powder of SiC or SiO₂ coated polymeric powder to ~190°C at a rate of 10°C/min for 30min in a rectangular aluminum mold (4"X 4"X1"). The mold was kept under the pressure of ~3000lbs

using a programmable MTP-14 compression molding machine. The test samples were cut precisely form the as-prepared panel and used for the morphological and mechanical testing.

Material	Compressive Strength [KPa]	Gain/Loss Compression [%] Modulus [MPa]		Gain/Loss [%]
Neat Foam	1200±50	0±50 - 30±3		-
1wt %SiC nanocomposite foam	2230±40	+86	34.1±4.5	+13
1wt %SiO ₂ nanocomposite foam	1418±45	+18	31.5±5.5	+4

Table 2. Compression test results of various samples.

To understand the effect of SiC and SiO₂ coating on polymeric particles the compression tests were carried for neat and nanocomposite foams. Two types of nancomposite (1wt % SiC and 1wt % SiO₂) samples and the neat samples were tested. Stress-strain curves for neat and nanophased samples shown in Figure. 8. Compression test data is presented in Table 2. It is observed in Figure. 8 that the compressive stress of the 1% SiC and 1% SiO₂ nano systems are about 86% and 18% respectively increased as compared with the neat expancel foam samples. The 1% SiC nanocomposite also shows 13% improvement in compressive modulus. This improvement are assigned to the increasing the interfacial bond between the nanoparticles and polymeric matrix.



Fig. 8. Compressive stress-strain curves are a) neat, b)1% SiO₂ and c) 1% SiC nanophased expancel foam

4. Alignment of acicular nanoparticles in thermoplastic polymers to improve the mechanical and antimicrobial properties of textile fibers

The use of nanotechnology in textile industry is rapidly growing because of their wide spread applications in healthcare, body armor, home furnishing etc. Nanoparticles such as silver, silver bromide, zinc oxide, titanium dioxide and copper oxide infused in synthetic polymers such as nylon and polypropylene can impart antimicrobial character to the textile fabrics for various applications (Sang et al., 2003; Zhang et al., 2001). Nylon-6, the semicrystalline polyamide known for its high toughness, tensile strength, low coefficient of friction and good abrasion resistance make it an ideal replacement for a wide variety of materials from metal to rubber. In the last few decades, there has been increased interest in antibacterial finishing on textile materials because of varieties of environmental pollutions. Ag is known to have a wide antibacterial spectrum and with high safety. It is a relatively non-toxic and natural inorganic metal and its nano size level makes its total surface area larger in an identity volume. Recently, Mecking and co-workers showed that hybrids of Ag nanoparticles with amphiphilic hyperbranched macromolecules were effective antimicrobial surface coating agents (Aymonier et al., 2002; Kim et al., 2007). Several salts of Ag and their derivatives are commercially employed as antimicrobial agents, as it is well known that silver ions and Ag-based compounds are highly toxic to microorganisms (Slawson et al.,1992; Zhao & Stevens,, 1998) showing strong inhibitory effects on as many as 16 species of bacteria including E. coli (Spadaro et al., 1974). Thus, nanoparticles of Ag have aptly been investigated for their antibacterial property (Sondi & Salopek-Sondi, 2004; Panacek et al., 2006; Morones et al., 2005; Baker et al., 2005). Nanoparticles of Ag also have been studied as a medium for antibiotic delivery (Li et al., 2005), and to synthesize composites for use as disinfecting filters and coating materials. However, the bactericidal property of these nanoparticles depends on their stability in the growth medium, since this imparts greater retention time for bacterium-nanoparticle interaction. Therein lays a strong challenge in preparing nanoparticles of Ag stable enough to significantly restrict bacterial growth.

Also, the use of carbon nanotubes as fillers has increased ever since their discovery as they are considered to be the ideal reinforcing agent for high-strength polymer composites because of their tremendous mechanical strength (higher Young's modulus, ~1 TPa which is comparable to that of diamond ~1.2 TPa and good elasticity), nanometer scale diameter, and high aspect ratio (Calvert, 1999; Salvetat et al., 1999; Yu et al., 2000). Carbon nanotubes (CNTs) have been used, in the last two decades, in applications ranging from DNA detection (Kouklin et al., 2005; Saugandhika et al., 2009) to nanorobots (Baxendale, 2003). The nano composite reinforcement is dominated by the collective behavior of the bundles rather than by the strength of the individual tubules (Ajayan et al., 2000). CNTs, which were of ~10-15 nm in diameter and about 5µm long were effective in load transferring mechanism than SWCNTs, as during loading the SWCNTs tend to pull out from the ropes (bundles), thus making load transfer difficult (Guang et al., 2006). Composites containing both noble metal nanoparticles and CNTs, in which nanoparticles are attached on the surface of the CNTs, have potential application in sensors, biomedical applications and heterogeneous catalysis (Yu et al., 2009). Ag decorated CNTs (Ag/CNTs) gained extensive attention due to their potential applications as catalyst (Guo & Li, 2005) 64], advanced materials (Wu, 2006), etc. Peng Cheng et al. proposed an approach for coating CNTs with Ag- NPs based on the wet chemistry reaction (Peng et al., 2006). Generally, a stable and uniform suspension of nanotubes in the polymer is required to obtain a fine dispersion and proper alignment of Ag coated CNTs within the fibers, which are instrumental for enhancement in structural, thermal and electrical properties of Ag/CNTs/Nylon-6 PNC fibers (Jeong et al., 2006). Ag coated CNTs (Ag/CNTs) nanoparticles were prepared by ultrasonic irradiation of Dimethylformamide (DMF) and silver (I) acetate (Aldrich) in the presence of CNTs. The asprepared Ag/CNTs were infused into the Nylon-6 polymer fibers through an extrusion process (*Wayne Yellow Label Table Top Extruder*) and these fibers were tested for their thermal, tensile and antimicrobial properties.

Tensile tests of single fiber specimens of the Nylon-6 and composites infused with Ag, CNTs and Ag/CNTs were carried out to estimate the increase in mechanical properties, such as strength and modulus.



Fig. 9. Tensile response of (a) Neat Nylon-6 (b) commercial Ag-Nylon-6 (c) CNTs-Nylon-6 (d) Ag/CNTs-Nylon-6

The results of tensile properties of the neat Nylon-6, 1.0 wt% commercial Ag/Nylon-6, 1.0 wt% CNTs/Nylon-6, and 1.0 wt% Ag/CNTs/Nylon-6, are and shown in Figure 9. The ultimate tensile strength values for neat Nylon-6, 1wt% commercial Ag-Nylon-6, 1wt% CNTs-Nylon-6, and 1wt% Ag/CNTs-Nylon-6 fibers were found to be about 240 MPa, 313 MPa, 339 MPa and 414 MPa, respectively. The tensile modulus values for neat Nylon-6, 1wt% commercial Ag-Nylon-6, 1wt% CNTs-Nylon-6, and 1wt% Ag/CNTs-Nylon-6 fibers were found to be about 0.84GPa, 2.73GPa, 5.05GPa and 3.76 GPa, respectively The tensile strength and modulus of the Nylon-6 infused with Ag/CNTs is 172% and 447% higher than the neat Nylon-6 polymer fibers. As expected we observe the highest percentage increase of modulus (650%) and relatively low (141%) increase for 1wt% CNT-Nylon-6. The significant improvement (172 and 447%) of the mechanical properties of the thermoplastic polymer by such 1wt% percentage of Ag/CNT filler is remarkable when compared with the other thermoplastic polymer composite fibers. For instance, in the recent work on polypropylene/F-SWNT composite fibers, the much higher loading of F-SWNTs (10 wt.%) was shown to yield a significantly lower tensile strength enhancement value (125%) (Daneesh et al., 2006).

We have also observed the high tensile strength of 413 MPa for 1.0 wt% loading of Ag/CNTs into Nylon-6. This measured strength value for nanocomposite fiber is more than 172% higher than that of the neat Nylon-6 which indicates the exceptional load bearing capability along with high elongation (35%) of Ag/CNTs and their potential applications in structural composite materials. In comparison with the 1.0 wt% Ag/CNTs/Nylon-6 composite fibers showing the higher tensile strength as 1.0 wt% CNTs/Nylon-6 samples, the former demonstrate better % elongation at break (Figure 7) which overall gives the best combination of mechanical properties among the Nylon-6 composite fibers we have studied. This conclusion is supported by comparison of tensile modulus values observed for neat Nylon-6, and 1wt% Ag//Nylon-6, which are 0.84 GPa and 2.73 GPa respectively. Such significant improvement of tensile modulus can be attributed to the infusion of high strength Ag/CNTs, their alignment in extrusion direction of Nylon-6 polymer fibers (Vijaya, et al., 2009 and 2008; Mahfuz et al., 2005), and the fact that nanotubes/particles do act as nucleation sites for crystallite formation. There are two different mechanisms acting in parallel to account for these results. We have also observed the decrease of elongation (9.6%) by infusion of only CNTs [(Khabashesku et al, 2006; Ignac, 2009; Feng et al., 2005). We know that the strength can be increased by infusion of CNTs in Nylon-6 fiber through melt extrusion process by alignment of CNTs in fiber direction (Vijaya et al., 2009 and 2008; Mahfuz et al., 2005). And also as explained in earlier section the strain to failure can be increases by infusion of smaller size nanoparticles in the polymer (Jeffrey et al., 2005; Mahfuz et al., 2007). In the present case the combination of smaller Ag nanoparticles coating on CNTs leads to increase in strength and stain to failure

5. Development of shear thickening fluid for liquid body armor applications.

Shear thickening is a non-newtonian flow behavior observed as an increase in viscosity with increasing shear rate or applied stress (Barnes, 1989). This phenomenon can occur in colloidal dispersions. In more concentrated colloidal suspensions have been shown to exhibit reversible shear thickening resulting in large, sometimes discontinuous increases in viscosity above a critical shear rate. Two main causes of reversible shear thickening have been proposed: The order-disorder transition [(Hoffmann, 1972, 1974 & 1983; Boersma, 1992; Laun et al., 1992) and the "hydrocluster" mechanism (Bender & Wagner, 1995 & 1996; Phung et al., 1976; Melrose et al., 1996; Farr et al., 1997; Brady et al., 1988). This transition from a flowing liquid to a solid-like material is due to the formation and percolation of shear induced transient aggregates, or "hydroclusters," that dramatically increase the viscosity of the fluid. Recently Wegner's group and U.S .Army research lab developed a body armor using shear thickening fluid and Kevlar fabric (Young et al., 2003). These research results demonstrate that ballistic penetration resistance of Kevlar fabric is enhanced by impregnation of the fabric with a colloidal shear thickening fluid. Impregnated STF-fabric composites are shown to provide superior ballistic protection as compared with simple stacks of neat fabric and STF. Comparisons with fabrics impregnated with non-shear thickening fluids show that the shear thickening effect is critical to achieving enhanced performance. In the present investigation we report on the synthesis of STF using sonochemical method, which can be potentially used for the body armor applications. Many researchers have used various techniques to prepare the shear thickening fluid. Acoustic cavitations technique is one of the efficient ways to disperse nanoparticles into the liquid polymers. In this study we have synthesized a shear thickening fluid in a single step reaction through high power ultrasound

technique, fabricate STF/fabric composite and characterize it for stab resistance applications. The rheology test results show that as-prepared STF sample exhibits shear thickening behavior. This behavior is very much evident as seen from the graph in Figure 10. The sample viscosity changes from ~ 20 Pa.S at shear rate of 5/S to 410 Pa.S at 12/S shear rate before reversal trend is seen. Continuous increase in sample's viscosity at low and very narrow shear rates range clearly confirm that the sonochemical mixing before evaporation drastically improves the shear thickening effect.



Fig. 10. Rheology graph for as prepared STF sample

Figure 11a shows the drop tower stab performance of neat Kevlar and STF/Kevlar composite targets for the knife and spike threats. As seen in the graph for the knife threat the penetration depth increases as the impact energy increase. STF/Kevlar composite target exhibit slightly less penetration depth and better stab resistance compared to the neat Kevlar target for low values of impact energy. At impact energy around 8 joules both targets reach maximum penetration depth of 5 witness papers. For the spike threat, as impact energy increases, depth of penetration into the backing material also increases. The STF/kevlar composite target exhibits significantly better stab resistance as compared with the neat kevlar target. The neat kevlar target exhibits maximum penetration of 5 witness papers at all impact energy levels. In contrast, STF/kevlar composite only penetrated through 1 witness paper at impact energy of 2.7 Joules and continued to resist the penetration, then showed maximum penetration of 5 witness papers at impact energy of ~ 8 Joules.

The results for neat nylon and STF/nylon composites stab testing for the knife and spike threats are presented in figure 11b. The results show the same trend as impact energy increases, depth of penetration into the backing material also increases. The STF/nylon composite target demonstrates slightly less penetration depth than the neat nylon target for the knife stabbing test.

As seen in the graph STF/Nylon composite target shows only 2 penetrated witness papers at impact energy of 2.7 Joules and when the impact energy reached a value of 5.4 Joules 3 witness papers were penetrated, the fourth witness papers penetrated at impact energy of 8.1 Joules and after that all 5 witness paper were penetrated for higher impact energy levels.

On the other hand the neat nylon target showed maximum penetration of 5 witness papers at impact energy of ~ 8 Joules. The results for the spike threat showed a significant improvement of the stab resistance of the STF/nylon composite target over the neat nylon target with just one penetrated witness paper in the first impact energy level of 2.7 Joules. The neat nylon target did not show any resistance for the spike stab testing with maximum of 5 witness paper penetrated for all impact energy levels. Dynamic stab test results show a significant improvement of target stab resistant and protection in STF/Fabric composite targets compared to neat fabric targets for both spike and knife threats.



Fig. 11. Dynamic stab test results for (a) neat Kevlar and STF/Kevlar composite (b) neat nylon and STF/nylon composite

6. Conclusions

Application of high intensity ultrasound irradiation is proven to be a versatile technique for synthesis, dispersion, and modification of nanoparticles. We have shown here that high intensity ultrasund can be used in synthesis of nanoparticles, modification of surfaces or uniform dispersion various nanoparticles depending on the solvent, precursor and resin system. In case of WO₃ nanoparticles, the high density commercial WO₃ nanoparticles are modified to porous nanoparticles and reduced the density and incresed the dispersion in epoxy. The high resolution TEM micrographs show that porous particles well dispersed in the epoxy resin when compared to nonporous high density nanoparticles. These effect were observed in increasing the their mechanical strength of the polymer. We have also shown that the dispersion and synthesis of naoparticles can increase the mechanical properties which will ultimately leasd to the high structural applications. The other aspect of nanocomposite fabrications is curing. The room temperature and microwave curing techniques were also used and shown the applications of nanoparticles in curing with microwave irradiation, The focus is to evaluate the mechanical properties of the neat EPON-862 and CNTs infused EPON-862 nanocomposites to study the fast curing microwave method as good as or better than the prolonged curing regular oven heating method. Improvements are observed for all samples with CNTs infusion in EPON-862 resin irrespective of curing methods. The compressive modulus/strength is increased about 28.57%/ 5.5% for MWC EPON-862/ 0.2wt%CNTs respectively as compared to the neat EPON-862 TC and TPC. These results are significant when consider the timesavings.

The coating of nanoparticles on various sufraces including CNTs and polymeric spheres were also shown. Mechanical tests also indicate that there is a significant increase in strength and modulus about 16% and 98% respectively. This technique can be applied to the other commercially available high density nanoparticle to reduce their sizes for better dispersion in epoxy resin systems for structural applications. High intensity ultrasound is also used in situ synthesis of Fe₃O₄ and Ag nanoparticles on CNTs. Flexural stress-strain results also indicate 50% increase in strength and 30% increase in modulus. TEM shows improvement in dispersion of CNTs in Epoxy system with magnetite coating. Ag/CNTs hybrid nanoparticles were synthesized using sonochemical technique. Neat Nylon-6, commercial Ag, pristine CNTs, and Ag/CNTs infused Nylon-6 polymer composites were fabricated using single screw melt extruder. TEM studies reveal that Ag nanoparticles were uniformly coated on CNTs surfaces and were non-covalently attached through van der Waals forces. The improvement in ultimate tensile strength and elastic modulus is attributed to the alignment of the Ag/CNTs nanoparticles along the direction of extrusion. The increase in thermal stability and crystallinity of Ag/CNTs infused Nylon-6 PNC is correlated with the better cross linking between the nanoparticles and the polymer matrix. The in-situ 1% Ag/CNTs Nylon-6 nanocomposite fibers were demonstrated to have excellent and promising antimicrobial activity as compared to the commercially available Ag nanoparticles, pristine CNTs and neat Nylon-6. It is also noteworthy to mention that this sonochemical synthesis technique can be used to synthesize Ag/CNTs composites in bulk quantities. This technique is also tested to coat uniformly CNTs SiO₂ or SiC on expandable microspheres. These foam materials can be used in many light weight high strength applications. Quasi Static compression test results indicate that there is a significant increase in compressive strength (45-51%) and modulus 20-40% as compared to neat system. This method can be efficiently used to synthesize shear thickening fluid as well with improved rheological properties and it is developed to prepare STF/ethanol solution in a single step. STF/fabric composites targets exhibit better stab resistance as compared neat fabric targets, this demonstrate that the impregnation of the fabric with a shear thickening fluid have enhanced the fabric performance for body armor applications. The flexibility and thickness of STF/fabric composites are comparable to the neat fabrics.

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Photochemically Implemented Metal/Polymer Nanocomposite Materials for Advanced Optical Applications

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1. Introduction

Nanocomposite materials metal/polymer combines together the properties of several components. Nowadays, they are regarded as promising systems for advanced functional applications (Armelao et al., 2006). In view of this, the incorporation of nanoparticles into polymer has opened the way to a new generation of materials exhibiting unique electrical, optical, or mechanical properties which make them attractive for applications in areas like optics (Jin et al., 2001; Ung et al., 2001), photoimaging and patterning (Tizazu et al., 2009; Stranik et al., 2010), sensor design (Shenhar and Rotello, 2003), catalysis (Vriezema et al., 2005), and as antimicrobial coatings (Aymonier et al., 2002; Sondi and Salopek-Sondi, 2004).

Research in novel methods to prepare metal nanocomposite materials has been greatly stimulated due to their attractive properties and promising applications. One of the main interests of metal nanoparticles stems from their unique physical properties which can be addressed by the chemical control of their shape and size (El-Sayed, 2001; Eustis and El-Sayed, 2006). Amongst them, gold, silver and cooper with nanometer size, have been the focus of great interest because these nanoparticles exhibit a very intense absorption band in the visible region due to their surface plasmon resonance.

Metal/polymer nanocomposites can be prepared by two approaches. The first one involves metal nanoparticles dispersion in a polymerizable formulation, or in a polymer matrix. In this case, the reduction of metal ions and polymerization occur successively hence the aggregation of nanoparticles that makes this synthetic procedure often problematical. In the second approach, nanoparticles are generated in situ during the polymerization to avoid agglomeration. The polymerization reaction and the synthesis of nanoparticles that proceed simultaneously were the subject of extensive studies.

Another technique consists in polymerizing the matrix around a metal nanocore by using chemically compatible ligands (Mandal et al., 2002) or polymeric structures (Corbierre et al., 2001).

In all cases, the high-performance of nanomaterials depends on the controlled distribution of uniformly shaped and sized particles. Therefore, the development of synthetic strategies to control particles growth and/or agglomeration during nanocomposite fabrication appears quite obviously as a key challenge.

Photochemical reduction by irradiating a dye sensitizer in the presence of metal ions provides a convenient way to produce nanoparticles embedded in polymer (Balan et al.,

2008; Korchev et al., 2004; Sangermano et al., 2007; Sudeep and Kamat, 2005; Yagci et al., 2008). In this context, the photoinduced synthesis has many advantages since it combines the characteristic features of light activation i.e. versatility and convenience of the process, high spatial resolution and reaction controllability (intensity and wavelength), with the simplicity of the colloidal approach. Various photo-induced synthetic strategies to obtain metal nanoparticles in a variety of conditions have been described by Sakamoto et al. (Sakamoto et al., 2009). However, photoassisted processes allowing the generation of polymer/metal nanocomposites that were introduced very recently are still in demand of further investigation.

2. Materials and methods

The absorption spectra were recorded using a Perkin-Elmer Lambda 2 spectrophotometer.

Photochemical reactions were carried out under irradiation at 532 nm with a cw laser VERDI from Coherent. The progress of the reactions was monitored via UV-Vis absorption spectroscopy.

Photopolymerization kinetics was studied in situ by real-time FTIR with an AVATAR 360 spectrometer from Nicolet. The formulation was sandwiched between two polypropylene films (10 μ m thick), deposited on a BaF2 pellet. Flood exposure during FTIR measurements was performed using a laser diode (type Cube from Coherent) emitting at 532 nm with an average intensity 5 mW/cm². The conversion rates were deduced from the progressive disappearance of the vinyl C=C stretching vibration band at 1630 cm⁻¹. Rp – the rate of polymerization - is defined as the maximum of the first derivative of the conversion vs. time curves. Usually, it is measured at the early time of the polymerization when the monomer concentration remains close to the initial bulk concentration ([M]⁰)

For recording holographic gratings, a typical setup of four-wave mixing based on a frequency-doubled cw YAG laser emitting at 532 nm (s-polarization) described earlier was used (Lougnot and Turck, 1992; 2002). The two arms of the interferometer were equipped with a spatial filter and the fringe visibility could be set with the help of a polarizing beam splitter and a system of half-wave plates. A low-intensity He-Ne laser beam ($\lambda = 633$ nm, 0.5 mW) placed at the Bragg angle corresponding to the spatial period of the grating, was used for real-time monitoring of the grating formation. The diffraction efficiency was calculated as $\eta = I_{\text{Diff}} / (I_{\text{Tr}} + I_{\text{Diff}})$ where I_{Tr} and I_{Diff} are the intensities of the transmitted and first order diffracted beams, respectively.

A specific device was developed to characterize holograms. It allows the record to be interrogated by a reading laser diode emitting at 633 nm with incidences covering a \pm 10° angular window on both sides of the Bragg incidence. The curve showing the actual diffraction efficiency as a function of $\Delta \theta'$ exhibits the well-known squared cardinal sine shape. It was thus, possible to use the Kogelnik's (Kogelnik, 1969) relationship for further calculation of the modulation of refractive index (Δn) and the effective thickness of the gratings (d).

The light energy needed for the input and output of the necessary information depends on the efficiency of the holographic recording material. The holographic sensitivity means a quantity inverse to the input energy (or energy density) at which the necessary output signal level appears (Collier et al., 1971). In a way, it measures the build up rate of a hologram. If the visibility is assumed to equal unity, the holographic sensitivity per unit area G (in cm²/J) expressed as follows (Carré and Lougnot, 1990):

$$G = \eta^{1/2} / I_0 t$$
 (1)

where I₀ is the power density in the two beams and t, the holographic exposure.

Transmission electron microscopy (TEM) was used to characterize the size and shape of Ag nanoparticles. Samples were sliced down by means of a microtome (LKB model 8800) and placed onto the copper grid. TEM measurements were carried out using a Philips CM20 instrument with LaB6 cathode. The gratings were also examined by a FEI 400 Scanning electron microscopy (SEM) and an atomic force microscopy (AFM) using a Pico Plus instrument from Molecular Imaging. After disassembly of the samples, the free surfaces of the records were analyzed in tapping mode with a Si_3N_4 tip the resonance frequency and spring constant of which were 100 kHz and 0.6 Nm⁻¹, respectively.

The precursor of metal nanoparticles was silver nitrate (ACS Reagent 99 % from Aldrich). It was added to the formulation as a fine powder and upon stirring, one hour before use. The formulations used in this work contained a liquid acrylic multifunctional monomer (typically, pentaerythrytol triacrylate, PETA from Cytec, Polyethyleneglycol 400 diacrylate, SR 344 from Sartomer and/or Bis-phenol A diacrylate, Ebecryl 600, from Cytec). The initiating system was based on a photosensitizer absorbing in the yellow-green range (Eosin Y) and an electron donor (methyldiethanol amine – MDEA - or ethyl-2-dimethyl amino-4-benzoate – EDMAB). These products were purchased from Sigma Aldrich and used as received.

The precursor of sol-gel materials was 3-[(MethAcryloxy)Propyl] TriMethoxySilane (MAPTMS). It was purchased from Aldrich and used as received.

3. Results and discussion

The present work reports a strategy to produce a nanoparticles-embedded polymer through a photoinduced one-step one-pot method. In this approach, a system combining a visible photosensitizer - Eosin Y dye (Scheme 1) and an electron donor - N-methyl diethanolamine (MDEA) was used to photogenerate Ag nanoparticles and to photoinitiate the free radical polymerization of a multifuctional acrylate monomer.



Scheme 1. Structure of Eosin Y disodium salt

Compared to the prior state of the art, the major innovation lies in the use of visible light to initiate both polymerization of the monomers and reduction of the metal nanoparticles precursor (silver cations) at the same time (Balan et al., 2008; 2010).

In short, this mechanism involves:

- i. the photogeneration of amine-derived initiating radicals (Amine⁺⁺),
- ii. the reduction of silver cations by the aminyl radical produced by the previous reaction,

iii. the initiation of radical polymerization of the monomer binder.

Sens + $hv \rightarrow$ Sens *	
Sens* + Amine → Sens'- + Amine'+	(i)
Amine [•] + → Amine [•] + H ⁺	
Amine' + $Ag^+ \rightarrow X + Ag_0$	(ii)
Amine' + Monomer \rightarrow Living polymer radical'	(iii)

3.1 Fabrication of silver nanoparticle embedded polymer

A formulation of SR 344 – 80 % and E 600 – 20 % monomers containing Eosin Y (0.1 wt %), MDEA (3 % wt) and AgNO₃ (1 wt %) was photopolymerized upon irradiation at 532 nm (2.5 mW cm⁻²). The conversion of acrylate double bonds was monitored from the decrease of the IR band at 1630 cm⁻¹. The conversion rate of this formulation was compared with that of a reference sample without AgNO₃ (Figure 1). Both samples show a similar rate of polymerization (within experimental error limits) with a maximum conversion degree leveling off at ca 80 %. This well-known effect is due to the crosslinking process. In fact, high crosslink density results in a gel-effect and the entanglement of living polymer chains sets a limit to the extent of conversion (Mehnert et al., 1997).



Fig. 1. Real-time FTIR kinetic conversion curves for visible curing at 532 nm of resins with and without particles (Insets: View of 30 μ m thick samples with and without nanoparticles after curing)

It is worth of notice that addition of Ag⁺ did not perturb the photopolymerization kinetics (Figure 1). On the contrary, the in situ synthesis of silver nanoparticles concomitantly with the photopolymerization process was observed to have an unexpectedly favourable effect on the rate of polymerization (Rp) (for instance, after a 100 s exposure, the conversion ratio are 55% and 80% in the absence and in the presence of nanoparticles, respectively). In the presence of metal nanoparticles, the polymerization started after a short inhibition period (ca 5 s), the conversion leveled off at a slightly higher value (83 % instead of 75 %) and above all, the Rp

was accelerated by a factor of 1.9 (in the presence of metal nanoparticles Rp is 2.6 M.l⁻¹.s⁻¹ and without particles, 1.4 M.l⁻¹.s⁻¹). Therefore, the generation quantum yield of MDEA• was sufficiently high to enable both free radical photoinitiation and photogeneration of Ag nanoparticles. Moreover, after 5 min exposure, the reference sample turned from pink to colourless whereas the sample with Ag⁺ turned from pink to yellowish (inset Figure 1).

The absorption spectrum of the sample underwent important changes during visible irradiation (Figure 2). The absorption band of EO²- faded off progressively while the surface plasmon resonance developed in the 350-500 nm region. This band exhibited a maximum wavelength at 437 nm with a FWHM of ca 115 nm.



Fig. 2. Time evolution of the absorption spectrum of the resin during photopolymerization EO²⁻/ MDEA / AgNO₃, (0.1 / 3 /1 wt %)

Careful analysis of the absorption spectrum over the illumination period clearly reveals a process corresponding to the photobleaching of EO²⁻ with the concomitant growth of the surface plasmon band.

The bright field TEM micrograph of a silver-nanocomposite is shown on Figure 3. Throughout the photoreduction process, the symmetrical shape of the surface plasmon band denotes a very narrow size-distribution of the silver nanoparticles photogenerated in the polymer matrix.

Electron microscopy analysis of the nanocomposite material confirmed the formation of monodisperse spherical metallic particles in the nanometer range size. Analysis of a population of ca. hundred particles from a portion of the grid indicated that their average diameter was 5.0 ± 0.7 nm. They were homogeneous in size and no agglomeration was observed. Such a homogeneous distribution can be accounted by the stabilizing effect of the monomer matrix. Through its acrylate functions, the monomer can easily adsorb on the nanoparticle surface. In this respect, the capping effect of unsaturated long-chain agents was previously reported by Wang et al. (Wang et al., 2002), who correlated the size of silver particles with the number of available double bonds in the chain.



Fig. 3. TEM image of silver nanoparticles embedded in a polyacrylate matrix, with the corresponding size distribution

3.2 Silver /hybrid sol-gel nanocomposite

Polymer matrixes suffer from intrinsic limitations due to the physical properties of the material: low refractive index, poor mechanical and thermal properties, dewetting or delamination effects limiting their use as thin films.

In this context, the sol-gel approach has proved to be an interesting alternative whenever the nanocomposite is to be used as a thin film coating (< 1μ m). Indeed, the presence of SiOH moieties favours adhesion of the film onto substrates such as Si or SiO₂ and the stabilization of nanosized metal particles.

Moreover, special attention has been paid to photopolymerizable hybrid sol-gel materials (Soppera and Croutxé-Barghorn, 2003.) since they allow the formation of hybrid organicinorganic materials by acid- or base-catalyzed hydrolysis and condensation of main group or transition metal alkoxides (Judeinstein, 1996). Due to the presence of a photopolymerizable function covalently bounded to the inorganic part, the specific advantages of photocuring are preserved: low temperature processing and spatial control of the polymerization reaction for photolithographic applications (Kärkkäinen, 2002).

The photochemical one-pot and one-step process was used in a hybrid sol-gel formulation to synthesize silver nanoparticles (Scheme 2), thus combining the advantages of the photochemical route to prepare nanocomposite materials with the unique properties of hybrid sol-gel matrix.

Silver particles/sol-gel nanocomposites films with open surface were prepared by photoinduced reduction of AgNO₃ and photopolymerization of a hybrid sol-gel host medium. Such highly crosslinked hybrid sol-gel films containing well-dispersed silver nanoparticles should arouse much interest in the world of optical waveguiding and coatings because of the potential of these new materials. Moreover, ultra-thin films of silver/sol-gel nanocomposites open new prospects in biomedicine and optoelectronics.

3.3 Applications of silver/polymer nanocomposites 3.3.1 Holographic recording

Holographers are in permanent demand for recording materials with more and more sophisticated technical features that justifies their great interest for metal/polymer nanocomposites. Furthermore, the development of periodically ordered metal structures should open up new vistas because of the possibility to couple propagative lightwave and surface plasmons, a promising field of research and development for designing diffractive optical elements with ultrahigh spectral dispersion (Mikhailov et al., 2007). And finally, the possibility to generate strings of metal nanoparticles embedded in a polymer matrix through a photochemical process that allows them to be manipulated seems to arouse much interest in the plasmonics community.



Scheme 2. Formation of silver / hybrid sol-gel nanocomposite

As regards holographic materials for storage applications, the introduction of an additional neutral component within the reactive formulation is a recurring concern for those who are developing new recording systems. It is based on the counter-diffusion of the components of the holographic formulation between the bright and dark regions under the influence of gradients of chemical potential induced by the photopolymerization of monomers. In the search for more and more innovative systems, Vaia et al. pioneered the use of nanoparticles (inorganics, organic polymers, metals or metal oxides) (Vaia et al., 2001). High diffraction efficiencies were reported in polymerizable blends containing nanoparticles (metals or oxides) synthesized beforehand (Nakamura et al., 2009; Sanchez et al., 2005). However, dispersing the nanoparticles in the reactive formulation was always mentioned as a critical step in the process.

Recently, the synthesis of new nanocomposites containing functionalized monomers and Au nanoparticles coated with ethyl 11-mercaptoundecanoate that allowed refractive index modulations exceeding 0.007 (i.e. diffraction efficiencies of ca 50 % in 20 μ m films) was reported (Goldenberg et al., 2008). The mechanism of refractive index contrast amplification in this new material was claimed to include both segregation of the components due to photoinduced gradients of concentration and interception of free radicals by Au nanoparticles. In contrast, and in spite of many works of scientists involved in this field, efforts aimed at fabricating spatially organized metal-polymer nanocomposites by an all-photochemical

fabricating spatially organized metal-polymer nanocomposites by an all-photochemical process were inconclusive and only weak diffraction efficiencies were reported. Following the line of the one-pot one-step synthesis of metal/polymer nanocomposites

described before, the holographic recording properties of acrylate formulations containing silver nanoparticles photogenerated in situ were investigated.

A formulation containing SR 344 (80%) and E 600 (20%) was used to record holographic gratings. The concentration of the sensitizer was adjusted so that the optical density of the samples was ca 0.6 at maximum (typ. 3×10^{-3} M). The holographic samples were sandwiched between two glass slides (28×76 mm) separated by a calibrated wedge. The thickness of the samples was either 23-24 µm or 45 µm, depending on the wedge used. The polymerizable formulations were prepared 24 hours before use and stored at room temperature in dark conditions.

According to the theory of holography, the gratings with spatial periods of ca 1 μ m and thickness of 16 or 30 μ m are Bragg volume gratings (Collier et al., 1971) only 0 and -1 orders were observed in the diffraction pattern. The angular dependence of the holographic response of the gratings showed excellent agreement with the Kogelnik analysis for thick phase gratings (Kogelnik, 1969).

An example of holographic sensitivity curves without and with silver nanoparticles is shown on Figure 4. The holographic sensitivity and efficiency at maximum of the gratings and the refractive index modulation achieved are presented in table 1 as a function of the recording conditions.

In this work, the reference system was deliberately selected because of its poor recording performances. It is characterized by a limited potential in terms of available index modulation that is related to the use of a mixture of two acrylic difunctional monomers and a tertiary amine generating EDAB-derived aminyl radicals that are reputedly mediocre initiators of polymerization (Pyszka and Kucybała, 2008). In such a formulation, the fate of silver nanoparticles is to undergo spatial segregation under the influence of driving forces resulting from differences of local properties between dark and bright fringes. Amongst the possible causes for this segregation, one can mention gradients of photoreduction rate of silver cations or gradients of crosslinking degree of the monomers, that both replicate the spatial distribution of the actinic light in the incident interference pattern.



Fig. 4. Holographic sensitivity curve derived from holographic recording results of sample 1 without Ag^+ (a) and sample 3 with 1% w/w Ag^+ (b) in Table 1 with the model of eq. (1)

A dramatic improvement of the recording characteristics of the formulation containing silver cations was observed. The amplitude of the available modulation of refractive index was much larger while the holographic sensitivity increased up to a hundredfold with [Ag⁺] = 1 % w/w. There is no doubt that the presence of silver nanoparticles photogenerated in situ is the key factor that is behind the change in the recording properties. However, it is worth of notice that a twofold increase of the concentration in silver cations did not improve the recording process further: the holographic efficiency increased by some 20 % while η_{max} decreased slightly.

The results reported in table 1 reveal also the influence of both the chemical and photonic parameters on the diffraction efficiency at maximum and the holographic efficiency (Balan, 2009). In the presence of silver, addition of increasing amounts of coinitiator (EDMAB) results in an important acceleration of the recording process. This observation is mainly accounted for by the increase of the photoreduction quantum yield of Eosin in its triplet state by EDMAB (Noiret et al., 1994).

Sampe	EDMAB	Ag+	Total	Exposure	η_{max}	Δn	G (cm ² /I)
	(11)	(⁷⁰ w/w)*	(mW/cm ²)	(5)	(%)	(x 10-5)	(CIII-7J)
1	0.4	0	20.8	180	8.9	121	0.13
2	0.4	0	41.8	240	16.9	185	0.12
3	0.4	1	10.0	60	52.7	290	12.2
4	0.4	1	10.0	15	41.1	265	12.3
5	0.2	0.5	5.0	150	68.1	308	4.2
6	0.2	0.5	10.0	100	69.2	303	3.9
7	0.2	0.5	20.0	60	80.0	376	2.8
8	0.2	1	10.0	60	48.7	300	4.8
9	0.2	1	20.0	30	72.5	329	3.6

(*) 0.5% w/w = 0.024 M; 1% w/w = 0.059 M

Table 1. Influence of the chemical and photonic parameters on the holographic sensitivity, diffraction efficiency at maximum of the gratings and refractive index modulation

Table 1 shows also that increasing the recording fluence always goes along with an increase of the diffraction efficiency at maximum but also with a decrease of the holographic efficiency. This behaviour is to be interpreted in terms of coupling between chemical reactions generating active species involved in the modulation of refractive index and physical processes responsible for the segregation of the components of the holographic formulation. The higher the fluence used to record the holographic grating, the faster the recording process but the less efficient is the segregation process (Samui, 2008).

Since the concentrations of Ag⁺ used in this work were quite small, the increase of refractive index modulation cannot be only accounted for by the presence of silver nanoparticles. Clearly, indirect physical and chemical effects of the nanoparticles must be invoked. Due to their strong interaction with nucleophilic groups, they are able to modify the polymerization kinetics and as an indirect consequence, the composition and morphology of the copolymer formed at the local scale. Given the difference of chemical structure and refractive index between the comonomers used ($n_{E600} = 1.548$ and $n_{SR344} = 1.466$), only a 1 %-modification of the copolymer composition between bright and dark areas of the record induces an increase of refractive index modulation of ca 150 10⁻⁵.

Analysis of the records by AFM, SEM and TEM AFM

Figure 5 shows the AFM characterization of two samples obtained with formulations without particles and with $1\% \text{ w/w Ag}^+$, respectively.



Fig. 5. AFM images obtained in tapping mode of holographic records without Ag⁺, (topography (a), phase (b), cross-section (inset)); and with Ag⁺, (topography (d), phase (e), cross-section (inset)) (Reprinted with permission from ref Balan et al., 2009. Copyright 2009 ACS)

The samples were disassembled before analysis and the free surface was kept for 24 h under vacuum to obtain a complete release of constraints stored in the polymer matrix.

Figures 5 a and b show the microstructures obtained at the surface of the sample containing no Ag⁰. On the topographic image (figure 5 a), the grating can be clearly observed. The amplitude of the relief is ca. 50 nm (inset figure 5 a). This surface corrugation results from the difference in the polymer structure between the bright and dark areas of the incident interference pattern. Such a surface corrugation was already observed in other photopolymerizable systems (Jradi et al., 2008). The period measured by AFM corresponds exactly to the period of the interference pattern (1 μ m).

In the case of Ag-doped material (figure 5 d, e), the grating was also clearly visible. The relief of the surface corrugation is of the same order as observed in the sample without nanoparticles, thus demonstrating that the polymer matrix is not significantly affected by
the presence of silver nanoparticles generated in situ. The contrast in the phase image is directly linked to difference in the polymer material structure. With the Ag-doped system, this contrast is more pronounced, meaning that the addition of Ag⁺ favours the apparition of gradients in the polymer structure. This observation is in agreement with the higher diffraction efficiency linked to the addition of Ag⁺. A close examination of the topography reveals a higher surface roughness in the case of the Ag-doped sample. The protuberances appearing in the phase image correspond to bright dots (figure 5 e); without hesitation, they can be attributed to silver nanoparticles since the mechanical interaction between the AFM tip and the metal nanoparticles emerging from the polymer surface is different than response on metal. Interestingly, the nanoparticules are not distributed homogeneously over the surface of the sample: Ag nanoparticles accumulate in the protruding regions of the grating. This spatial segregation is the key-factor accounting for the increase of holographic efficiency observed in doped samples.

SEM

Figure 6 shows micrographs recorded by scanning electron microscope (SEM) of two UVcured samples obtained with Ag⁺ and without Ag⁺ respectively. Clearly, silver nanoparticles induce physical changes in the polymer (morphology, free volume) and chemical changes (local composition of the copolymer formed in the presence of nanoparticules (Yagci et al., 2008).

Presumably, the refractive index change results not only from the segregation of the nanoparticles but also from important changes in the structure of the polymer at the molecular scale.



Fig. 6. SEM images of holographic records (a) without and (b) with 1% silver cations

TEM

TEM image (Figure 7), confirms without contest a patterned distribution of individual nanoparticles in the polymer matrix that form a grating with a period of ca 1 μ m. As shown in Figure 7 particles are spherical with an average diameter of 20 nm.

3.3.2 Polymer tips terminated by silver nanowires for sensors

In this application, a one step photochemical process was used to generate a silver/polymer composite tip at the end of an optical fiber. Such an integrated nanodevice should achieve great success in the fields of plasmonic, nanoscale electronic devices or biomedical sensors.



Fig. 7. TEM micrograph of the grating formed with silver nanoparticles

The simultaneous photo-reduction of silver and crosslinking photopolymerization involves amine-derived radicals generated from the reduction of the excited sensitizer in its triplet state by the electron-rich co-initiator molecules.

With a view to implementing at the end of optical fibers advanced optical functions that would take advantage of the unique properties of photogenerated metal nanoparticles, the reduction of silver cations was carried out using the light emerging from an optical fiber. The formulation developed for this purpose was sensitive to green laser light (typ. 532 nm).

The end of a freshly cleaved optical fiber was dropped into a formulation containing a photosensitizer (Eosin disodium salt, 0.5 % wt), a co-sensitizer (MDEA, 4 % wt), a silver salt (AgNO₃, 0.2 % wt) and a trifunctional monomer (PETA) (Jradi et al., 2010). Then, a green laser beam (532 nm) guided into the fiber was used to photo-reduce Ag+ cations; crosslinking photopolymerization involves amine-derived radicals generated from the reduction of the excited sensitizer in its triplet state by the electron-rich co-initiator molecules. As can be seen on figure 8, after careful solvent development, SEM analysis revealed the existence of silver nanowires bristling at the surface of the tip. The wires seemed to grow lengthwise from the top of the tip; their length ranged from 500 to 600 nm while their diameter was about 50 nm (see figure 8 c).

The mechanism of nanowires growth is still under investigation. However, the following points can be already considered for granted: silver nanoparticles located at the surface of the silver/polymer composite tips are prone to enhance the light field in their immediate vicinity and favour the nucleation and co-aggregation of silver nanoparticles that growth normally to the surface to generate silver nanowires. The anisotropic growth starts only from the small fraction of nanoparticles located at the polymer/solution interface and with such an orientation and size that the subsequent growth of the nanocrystaline structure is possible.

Of course, the great majority of metal nanoparticles, more or less deeply embedded in the polymer tip, do not meet these requirements, hence the low yield of nanowires. Because the surface plasmon field enhancement is higher in the regions corresponding to singularities, metal nanowires grow where the surface curvature is important. This process generates metal bumps at these sites, the tops of which form sharper and sharper singularities that amplify the anisotropy of the growing process. Therefore, the nanowires grow mainly lengthwise.



Fig. 8. Silver/polymer composite tip integrated at the end of an optical fiber and zooms of the extremity of the tip showing silver nanowires. Light Power = $2 \mu W$, exposure time = 5s (Jradi et al., 2010. Copyright 2010 Nanotechnology)

The question of controlling their spatial distribution and orientation and providing an efficient anchoring of the nanowiers at the polymer surface remains unanswered. It can be observed that the new route used here leads to Ag nanowires perpendicular to the polymer surface. The nanowires are produced at the extremity of the polymer microtip, e.g. in the irradiated area.

Quite interestingly, electron beam irradiation generates no surface electrostatic effects on such composite polymer tips even up to 30 kV. The presence of silver nanoparticles in the composite improves its surface conduction. This feature is of the highest interest for applications in optical connecting and optical fiber sensing. In particular, metal nanowires that are one-dimensional (1D) objects have attracted particular interest, due to their unusual behaviour in the fabrication of nanoscale electronic devices and investigation of quantified conductance and biomedical nanoaddressing. Furthermore, such silver/polymer nanowires could be used as efficient nano-antenna probes for scanning-near field microscopy (Frey et al., 2002).

4. Conclusion

The works described in this chapter report on the use of photopolymerizable formulations that are capable of generating metal nanoparticles in situ and spatially control their distribution and orientation through photochemical activation. The process used avoids handling dry metal nanoparticles and aggregation that takes place during dispersion in a liquid formulation. Quite interestingly, the presence of metal nanoparticles was observed to accelerate and improve the crosslinking of multifunctional monomers forming the continuous polymer medium while the quantum yield of photobleaching of the sensitizer involved in the initiation process remained unaffected.

This system was used to record holographic gratings; it was observed that both the holographic sensitivity and the diffraction efficiency at maximum were significantly improved in the presence of particles. Obviously, the holographic efficiency of the photochemically assisted process depends on the coupling efficiency between the reaction generating nanoparticles and the photocuring of the polymerizable formulation. Electron microscopy reveals the presence of straight strings of metal nanoparticles in the middle of bright fringes of the holographic pattern.

This photochemical process was also used to develop silver /polymer composite tips at the extremity of optical fibers. In a further approach aiming at generating a single metal nanoparticle at the top of a polymer tip ended optical fiber, attempts are made at increasing the non-linear character of the photochemical reaction used to create nanoparticles with the help of chemical additives.

This process provides a very powerful tool to manipulate nanoparticles at the nanoscale and offers a versatile means to fabricate microoptical elements, the design of which involves a patterning of the spatial distribution of nanoparticles. It opens up fascinating prospects in the field of microoptics and plasmonics.

5. References

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PET-MMT and PET-PEN-MMT Nanocomposites by Melt Extrusion

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1. Introduction

Polymer nanocomposites have attracted a great deal of interest in the scientific and industrial fields because of remarkable improvements achieved in the physical and mechanical properties at very low filler loadings. For example, the diffusion of gas molecules is largely retarded by the presence of randomly oriented clay particles.

These new class of materials can be obtained by means of two main processes: in-situ polymerization of monomers in the presence of nanoparticles and the use of polymer processing techniques such as extrusion [Okamoto, M. 2006 and Suprakas, S. R. 2003]. The use of clay particles to produce nanocomposites is a usual practice; however, clay has to be usually organically modified to induce affinity with the polymer matrix [Kráčalík, M. et al 2007; Vidotti, S. E. et al 2007]. The improvement of nanocomposite properties depends on different factors, for example, a good dispersion of clay particles in nano-scale within the polymer matrix. The nanocomposites obtained by melt extrusion require initially, an intercalation process of the polymer matrix. This process is diffusion-controlled and requires long residence times under the pressure buildup produced inside the extruder. However, high residence times or high screw speeds may conduce to polymer degradation. Therefore, optimum process conditions need to be investigated in order to produce high performance nanocomposites.

Moreover, it has been found that clay exfoliation may not be a sufficient condition to obtain optimum properties; clay platelets dispersion and polymer-clay interaction are also key features to consider.

In this chapter, poly(ethylene terephthalate)-montmorillonite clay (PET-MMT) and poly(ethylene terephthalate)-poly(ethylene naphthalene 2,6-dicarboxylate)-montmorillonite clay (PET-PEN-MMT) nanocomposites were prepared and characterized. Maleic anhydride (MAH) is used as the compatibilizing agent in the blend and its effect is also studied. In both nanocomposite blends, optimum processing conditions were investigated to achieve improved tensile properties. The preparation of the PET-PEN polymer matrix also requires special care since a transesterification reaction between these two polymers is induced by

the process; the transesterification (NET) reaction between PET and PEN is affected by temperature and residence time in the extruder; nevertheless the presence of clay particles was also found to affect this reaction. Regarding thermal properties, crystallization enthalpy was found to diminish in the clay presence, i.e. the clay restricts the crystallization of the polymer matrix. Finally, the rheological behavior of these materials is still far from being fully understood. An increase in the steady shear flow viscosity with the clay content has been observed for most systems while in some cases the viscosity decreases with low clay loading. Other important characteristic of exfoliated nanocomposites is the loss of the complex viscosity Newtonian plateau in oscillatory shear flow. Transient rheology experiments have also been used to study the rheological response of polymer nanocomposites. The degree of exfoliation is associated to the amplitude of stress overshoots in start-up experiments. Two main modes of relaxation have been observed in the stress relaxation (step shear) test, namely, a fast mode associated to the polymer matrix and a slow mode associated to the polymer-clay network. Rheology results are discussed and instantaneous stress relaxation curves are presented for the PEN, PEN-PET and PET-PEN-MMT systems. A Fourier Transform (FT) frequency response was obtained from the relaxation curves and compared to the linear oscillatory data, which leads to an extended frequency region. The results were modeled by a rheological equation of state which accounts for the structure formation-destruction dynamics during flow; this equation is presented in the theoretical section in full detail. Relaxation time spectra are presented and compared for both rheological tests, namely, instantaneous stress relaxation and linear oscillatory flow. Additional studies using scanning electron microscopy (SEM) are presented, which reveal the presence of a slip layer in capillary flow for nanocomposite as opposed to the unfilled system which may explain the viscosity decrease observed in these systems.

Still further investigation is required to assess the main reinforcement mechanism of the nanoparticles, since it is not clearly resolved whether exfoliation or good dispersion are required.

2. PET-PEN Transesterification reaction

The transesterification reaction that occurs between poly(ethylene terephthalate) and poly(ethylene 2,6-naphthalene dicarboxylate), PET and PEN respectively, can be represented by the following equation.

$$TET + NEN \frac{\dot{k}'}{\vec{k}} 2TEN \tag{1}$$

where: TET= terephthalate-ethylene-terephthalate, NEN= terephthalate-ethylenenaphthalene and TEN= terephthalate-ethylene-naphthalene. The equilibrium constant for this reaction can be expressed as:

$$K^{\prime\prime} = \frac{K}{K^{\prime}} = \frac{\left[\text{TEN}_{eq}\right]^2}{\left[\text{TET}_{eq}\right]\left[\text{NEN}_{eq}\right]}$$
(2)

where subscript "eq" refers to equilibrium reaction conditions.

Several authors have given attention to the kinetics of thistransesterification reaction describing it as a second order reversible reaction [Chen et al. 1996, Lee et al, 1999, Alexandrova et al. 2000].

However, the equilibrium constant was considered in those works as equal to one, which presumes that the reaction of equimolar amounts of thereactants leads to equal concentrations of molar fractions of the species when the transesterification reaction reaches equilibrium.

Based on the results above mentioned, the mechanism and kinetics of the transesterification reaction in poly(ethylene terephthalate) and poly(ethylene 2,6-naphthalene dicarboxylate) polymer blends was simulated using model compounds of ethylenedibenzoate (BEB) and ethylene dinaphthoate (NEN)[Alexandrova et al. 2000]. An additional investigation dealt with the actual melt extrusion of the blend below the critical reaction temperature in the extruder [Medina et al. 2004]

Prior to melt compounding in the extruder, the PET and PEN polymers were previously dried in a Cole–Palmer vacuum oven at 120 °C with-45mm Hg pressure during 10 h. Extrusion was carried out in a Haake-Rheocord 90 TW-100 twin-screw conical counter-rotating extruder of 331 mm length, with temperature profile of 230, 240 and 250 °C and screw speed of 30RPM. The resulting mixture was milled and placed in open glass ampoules, 2 g each. Sets of eight samples were immersed into a thermo-stated silicon oil bath at 300 and 320°C during defined time intervals. Thereafter, samples were cooled to room temperature. Solids obtained were dissolved in a 70/30 vol. CDCl₃ and CF₃COOD solvent mixture for ¹H NMR analyses. NMR spectra were obtained in a BruckerAdvance 400 spectrometer.

The formation of the TEN copolyester is depicted in figure 1. The transesterification kinetics was followed by measuring the integral intensities of the aliphatic proton signals for TET, NEN and TEN. As the reaction progresses, a copolyester is formed and this is evidenced as an intermediate signal (TEN) between those corresponding to TET and NEN. Values for the equilibrium constant were found to lie between 3.8-4, from which authors determined that the value of the equilibrium constant was four:

$$K^{\prime\prime} = 4K^{\prime} \tag{3}$$

It was also confirmed that heating the blend above 300 °C direct ester-ester exchange mechanism produces the TEN sequences with reversible second order kinetics. The reaction order was confirmed using pseudofirst order conditions with a 10-fold excess of either PET or PEN. Kinetics was followed by the limiting reactant disappearance, as well as the formation of the TEN product. Kinetic data obtained were treated in terms of first order kinetics, according to the following equation:

$$\ln \frac{\left[\text{NEN}\right]_0}{\left[\text{NEN}\right]} = \overline{k}t \tag{4}$$

A linear tendency of concentrations ratio versus time was obtained (not shown) for the PET/PEN blend with 10:1 mole ratio, indicating that the transesterification reaction in PET/PEN system is first order regarding either of the reagents (Same results were found when PEN was in excess). Thus it was concluded that the overall order of the reaction is second order.



Fig. 1. Proton MRN spectra of the formation of the TEN copolyester in the TET/NEN blend at different stages of the transesterification reaction

The influence of extrusion residence time and temperature on the kinetics of the transesterification reaction has been also studied using a 30 mm diameter co-rotating twinscrew extruder (Werner & Pfleiderer ZSK30) with a general-purpose screw configuration including two rows of kneading elements (15 elements by row and 5 mm width each) and L/D = 30 [Sánchez-Solís et al. 2005a]. Three extrusion profile temperatures and two residence times were studied: temperature profile 1 (262-265-269-267-270 °C), temperature profile 2 (230-281-278-282-280°C) and temperature profile 3 (273-291-290-290°C). The extent of transesterification, i.e. the percentage of naphthalene-ethylene-terephthalate blocks (NET) as compared to the total terephthalate-ethylene-terephthalate blocks (TET) and naphthalene-ethylene-naphthalene blocks (NEN) was derived by spectral deconvolution of the peaks corresponding to each group (see fig. 1) i.e. peaks at 4.9 ppm NEN, 4.8 ppm TET and 4.85 ppm NET (peak due to transesterification) were measured.

It was found that the kinetics of the transesterification reaction was different in profile 3 as compared to the other two profiles studied. Residence time affected in a negative way the production of NET groups (groups related to transesterification reaction) at profiles 1 and 2, while at profile 3 the effect was the opposite: percentage of NET groups increased with residence time. Finally, profile 3 was reported to produce more random copolymer structures during transesterification reaction, i.e. increasing the degree of transesterification leads to higher proportion of random sequences and thereby reducing blend performance [Chen et al. 1996; Lee et al. 1999], while the other two profiles produced more block copolymers.

Finally, the degree of transesterification has been reported to be reduced in the presence of clay particles [Sánchez-Solís et al. 2005b]. Moreover, the particles need not to be organically modified to cause this effect. The hydrophilic clay is highly incorporated in the polymer and presumably has a low concentration at the surface, as evidenced by contact-angle measurements. Show a predominantly hydrophobic character of the clay surface. This blend also presents a large solid-like behavior, which is further discussed in the rheology section.

3. Preparation of nanocomposites by melt extrusion

3.1 PET nanocomposites

Polymer nanocomposites can be obtained by two general routes: the first one is the polymerization of monomers in contact with the nanoparticles (in situ polymerization), and the second one implies the use of existing processing equipment to melt compound the nanocomposite. An example of the latter is reactive extrusion.

In the extrusion process, the nanocomposites are formed initially by intercalating the polymer chains inside the clay galleries gap; this intercalation is the initial step obtain full exfoliation of the clay. However, a complete intercalation requires low screw speeds with the consequent long average residence times within the extruder. This, however, can lead to polymer degradation. In order to avoid polymer degradation, different screw configurations, chemically modified clays or a combination of both can be used. Furthermore, clay exfoliation may not be a sufficient condition to obtain high performance nanocomposites, other factors like nanoparticle-polymer matrix interaction can be considered.

Production of PET-Montmorillonite clay nanocomposites by extrusion has been reported in the literature [Sánchez-Solís et al. 2003]. Additives such as Maleic Anhydride (MAH) and Pentaerythrytol (PENTA) were used to induce compatibility between hydrophilic clay and hydrophobic polymer matrix. MMT was chemically modified with a quaternarium ammonium salt. A co-rotating twin screw extruder (Werner & Pfleiderer ZSK30) was used to melt compound the nanocomposites. In this study clay concentrations up to 2% were considered because higher concentrations caused a decrease in the glass transition temperature. It was reported that crystallization temperature is reduced as a function of clay content; this effect is even more pronounced when additives are used during melt compounding. On the contrary, when the nanocomposites are produced by in-situ polymerization, clay content was reported to have little effect on the crystallization temperature [Ke et al. 1999]. Additives (MAH and PENTA) were reported to increase the crystallinity of the nanocomposites which resulted in superior mechanical properties [Sánchez-Solís et al. 2003] as will be discussed in the mechanical properties section.

The effect of modifying the MMT clay prior to melt compounding with PET by using additives such as alkylammonium chlorides from amines of various chain lengths as well as MAH and PENTA has also been reported [Sánchez-Solís et al. 2004]. The objective of using the alkylammonium chlorides is to impart the nanoclays with functional groups to enhance the polymer-clay interaction and thus facilitate the production of exfoliated and dispersed polymer nanocomposite systems. A Haake Rheocord 90 TW-IOO twin-screw conical counter-rotating extruder of 331 mm length was used for blending. Properties for these nanocomposites will be discussed in the following sections (4-6).

3.2 PET-PEN nanocomposites

The production of PET-PEN-montmorillonite clay nanocmposite blends by extrusion has been reported previously [Sánchez-Solís et al. 2005b]. A quaternary alkylammonium compound (octadecylammoniumchloride) and maleic anhydride were used to modify the surface properties of sodium montmorillonite clay particles. After this process, the particles were mixed with poly(ethylene terephthalate) (PET) and poly(ethylene naphthalene 2,6 dicarboxylate) (PEN) to produce blends whose properties were examined in detail. Blends were prepared in a Leistritz LSM34 corotating twin-screw extruder (Leistritz, Nuremberg, Germany) equipped with a volumetric feeder working under a nitrogen atmosphere to prevent moisture absorption and consequent hydrolysis or chemical degradation of the polyesters.

Preparation of the polymer nanocomposites was carried out at 90, 9 and 1 wt% PET, PEN and clay contents, respectively, with 50 rpm extruder screw rotational velocity (corresponding approximately to 2 min residence time). Three clay types were used in the blends: sodium montmorillonite clay (clay–Na+), maleic anhydride-modified clay (clay–MAH) and alkylammonium-modified clay with n-octadecylamineas precursor (clay–C18).

Glass transition temperature (Tg), crystallization temperature (Tc) and melting temperature (Tm) were measured for the three blends (Table 1). While crystallization and melting enthalpies are similar for PET-PEN/clay-Na+and PET-PEN/clay-C18, differences are observed in the clay-MAH blend. The latter has substantially lower enthalpies of crystallization and melting than those of the other systems. The melting enthalpy for this blend is even lower than those of neat polymers. These results indicate that crystallization is largely restricted and proceeds in a very slow manner, which leads to a large proportion of the amorphous phase with high transparency.

Sample	Tg (°C)	Tc (°C)	Δ Hc (J/g)	Tm (°C)	Δ Hm (J/g)
PET	71	-	-	242	40
PEN	116	-	-	258	36
PET-PEN	75	161	18	244	18
PET-PEN/clay-Na+	75	138	198	248	228
PET-PEN/clay-MAH	71	139	21	248	27
PET-PEN/clay-C18	75	143	185	247	216

Table 1. Thermal properties of PET-PEN/clay blends and neat polymers

Another important remark of this study is the fact that from contact angle measurements at the surface of extruded samples reveal that the particle concentration at the surface decreases with respect to that in the bulk, i.e. In spite of the fact that clay–Na+ is hydrophilic, the surfaces of all samples show a hydrophobic character. This will be discussed further in the morphology section.

4. Mechanical properties

4.1 PET-PEN blends

Mechanical properties of bottles made by injection blow molding after melt extrusion have been reported [Sánchez-Solís et al. 2005a]. Sample specimens were obtained from the bottles

in the longitudinal direction. The processing conditions to obtain bottles with high mechanical properties (tensile strength) were 270°C with 4 min processing time and PEN contents of 15-20%. With the maximum tensile strength obtained for the blend containing 15 wt % of PET. Bottles made from this blend had a tensile strength 2.6 times higher than pure PEN and 3.6 times that of pure PET indicating some synergistic mechanism.

Also, Young's modulus attains a maximum (2.3 times that of PET and 1.6 times that of PEN) when the PEN content is 15wt % at the mentioned processing conditions. Mechanical properties showed no direct relation with % transesterification.

4.2 PET-nanocomposites

Mechanical properties of bottles produced from PET-MMT clay nanocomposites have also been reported as mentioned in section 3.1 [Sánchez-Solís et al. 2003]. After melt compounding the nanocomposite, bottles were produced in an injection-stretch blowmolding machine AOKI in one step with a temperature profile of 275 °C at the feeding section and 320 °C at the injection nozzle, with mold temperature of 16 °C. Bottles were reported to be transparent with a slight brown coloring. Specimens for mechanical testing were cut out from bottles in the longitudinal direction. All specimens for testing have the same thermo-mechanical history so as to avoid the effect of sample degradation on mechanical properties. In this study clay particles did not showed complete exfoliation, nevertheless, the use of additives to improve polymer-particle affinity produced nanocomposites with superior mechanical properties. However, in some samples, improved mechanical properties were achieved without compatibility additives: 30% and 32% maximum enhancement in tensile strength and Young's modulus. These results indicate that an important issue to consider in preparing polymer nanocomposite is particle dispersion, which can be as important as exfoliation and polymer-clay affinity.

The effect of different modified MMT clays on the mechanical properties of PET nanocomposites has been given attention [Sánchez-Solís et al. 2004]. Specimens for mechanical testing were produced by injection. The clay was modified prior to melt compopunding with PET and different additives were used to modify the blend: Maleic Anhydride (MAH), Pentaerythritol (PENTA) and alkylammonium chlorides from amines of various chain lengths such as n-Decacylammonium, n-Dodecylammonium, n-Tetradecylammonium, and n-Octadecylammonium. It was found that the interlayer distance in the clay varied according to the additive used, however this interlayer distance did not show a direct relation to the amine chain length.

Mechanical properties of unmodified and chemically modified nanoparticles (with MAH and PENTA respectively) are discussed first. A direct relation between clay content and Young's modulus was found for the unmodified and modified clay. The rate of crystallization of the nanocomposites was reported to have a threefold increase as compared to pure PET, indicating that the nanoparticles have a nucleating effect. This increased crystallization affected directly to the mechanical properties producing nanocomposites with higher modulus than that of pure PET, but with reduced strain at break i.e. cristallinity generates more fragile materials. This was the general effect for the nanocomposites with modified clay using only one additive; in fact, PENTA modified clay produced the nanocomposite with highest Young's modulus and tension strength at 3% and 1% content, respectively. However when MAH modified clay was melt compounded with the polymer and PENTA was added. The resulting nanocomposite showed the highest tensile strength and deformation at break, indicating a synergistic mechanism between MAH and PENTA.

For the case of the amine modified clays, only two systems showed complete exfoliation one of which showed the highest tension strength and deformation at break (1% clay modified with n-Dodecylammonium) indicating that in this case, exfoliation plays a key role in obtaining superior mechanical properties. Molecular weight in all samples was reported to have little or no modification with clay addition.

4.3 PET-PEN nanocomposites

In the case of PET-PEN-MMT nanocomposites, three kinds of clays have been used: unmodified (clay-Na⁺), maleic anhydride (clay-MAH) and octadecylammonium chloride (clay-C18) modified clays. The effect of clay modification on the mechanical properties of the extrusion melt compounded nanocomposite has been reported [Sánchez-Solíset et al. 2005b]. A reduction of the tensile strength as compared to pure PET or PEN is reported, while strain at break increases (with respect to the value of pure PEN). The lowest tensile strength and strain at break values were reported for the blend made with clay-C18. This system was not exfoliated and the blend appears more fragile, hence confirming the lower compatibility of the ingredients of this blend when compared to those of the exfoliated clays (see Table 2).

	Tensile	Elastic	Strain	x-ray
	strength	modulus	at break	data
Sample	[Mpa]	[Mpa]	[%]	
PET	51	1447	917	-
PEN	70	1752	356	-
PET-PEN	50	1296	525	-
PET-PEN/clay-Na+	42	1369	663	Exfoliated
PET-PEN/clay-MAH	46	1383	756	Exfoliated
PET-PEN/clay-C18	38	1571	19	33.24 U

Table 2. Tensile Mechanical properties of PET-PEN-MMT nanocomposites and neat polymers

5. Morphology

Although morphology has not been extensively studied in PET-PEN-MMT nanocomposites there are some interesting results in this field, for example, Figure 2, shows three micrographs for pure PET (a), 1% (b) and 2% (c) Dodecylammonium modified clay [Sánchez-Solís et al. 2004]. In (a) PET morphology presents the typical ductile fracture with voids indicating high energy absorption. Sample (b) corresponds to an exfoliated sample (discussed at the end of section 4.2) where ductile fracture with multilayer formation is observed and matrix yielding is present. Sample (c) presents no exfoliation morphology, exhibiting irregularities and fracture occurring at various positions, indicating fragile fracture (as verified by the low strain at break value, 2.6%).

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Fig. 2. Micrographs showing the center strained region of tensile test specimens (a) pet, (b) PET+1% Dodecylammonium modified clay, (c) PET+2% Dodecylammonium modified clay

SEM was also used to explore the surface of a PET-PEN-MMT nanocomposite filament obtained by using a capillary rheometer with a die L/D = 20 (at 270 $^{\circ}$ C, 10 s⁻¹). A flexible peel of low molecular weight polymer was observed in the section of the filament exposed

to the wall die. Evidence of an internal slip layer is also observed. This may be the cause of the decrease in the shear viscosity observed when clay is added; this effect will be further discussed in the rheology section. This peel was not observed in the system with no added clay (See figure 3). An internal slip layer was also observed. [Calderas et al. 2009]



Fig. 3. SEM micrographs of the edge of the capillary filament. Left: PET-PEN blend. Right: PET-PEN blend with 1% clay.

6. Rheology

6.1 Theory

6.1.1 BMP constitutive equation

In this section, we discuss the predicting capabilities of constitutive equations to describe the rheological behavior of nanocomposite systems. Underlying mechanisms are the structural modification under flow and induction or formation of structures. An example of a constitutive equation which describes these processes is the BMP equation of state. This equation [Bautista et al. 1999; Manero et al. 2002] is written here in terms of a stress superposition according to:

$$\underline{\underline{\sigma}} = \sum_{i=1}^{N} \underline{\underline{\sigma}}_{i} \tag{5}$$

$$\underline{\underline{\sigma}}_{ii} + \frac{\eta_{0i}}{G_{0i}} \xi_i \Big(\mathrm{II}_{\underline{\underline{D}}} \Big) \underline{\underline{\sigma}}_{ii} = 2\eta_{0i} \xi_i \Big(\mathrm{II}_{\underline{\underline{D}}} \Big) \underline{\underline{\underline{D}}}$$
(6)

$$\frac{d}{dt}Ln\xi_{i}\left(\Pi_{\underline{D}}\right)^{\lambda_{i}} = 1 - \xi_{i}\left(\Pi_{\underline{D}}\right) + \beta_{i}\left(1 - \mathbf{B}_{i}\xi_{i}\left(\Pi_{\underline{D}}\right)\right)\underline{\underline{\sigma}}_{\underline{i}} : \underline{\underline{D}}$$
(7)

$$\xi_{i}\left(\Pi_{\underline{D}}\right) = \frac{\eta_{i}\left(\Pi_{\underline{D}}\right)}{\eta_{0i}}; \qquad \beta_{i} = k_{i}\lambda_{i}; \quad \mathbf{B}_{i} = \eta_{0i} / \eta_{\infty i}$$

$$(8)$$

Where $\underline{\sigma}_{i}$ and \underline{D}_{i} the stress and rate of deformation tensors, respectively; $\underline{\sigma}_{i}^{\forall}$ denotes the upper-convected derivative of the stress tensor; and λ_{i} , G_{0i} , η_{i} , η_{0i} stand for variable relaxation time, elastic modulus, viscosity function and viscosity to low shear rate respectively. $\xi_{i}(\Pi_{\underline{D}})$ are scalars that reflect changes in viscosity due to changes in the structure induced by flow. $\beta_{i}=k_{i}\lambda_{i}$ can be interpreted as an inverse of the energy associated to

the kinetics and structural mechanisms. The two characteristic times λ_{0i} , $\lambda_{\infty i}$ are Maxwell relaxation times to low and high shear rate respectively.

For a mono modal model (i = 1), the BMP [Bautista et al. 1999, 2002; Soltero 1999, Manero et al. 2002, 2007; Escalante et al. 2007; Calderas et al. 2009; Herrera et al. 2009, 2010] model is defined by the following equations:

$$\underline{\underline{\sigma}} + \frac{\eta \left(\mathrm{II}_{\underline{D}} \right) \nabla}{G_0} \underline{\underline{\sigma}} = 2\eta \left(\mathrm{II}_{\underline{D}} \right) \underline{\underline{D}}$$
(9)

$$\frac{d}{dt}Ln\eta\left(\Pi_{\underline{D}}\right)^{\lambda} = 1 - \frac{\eta\left(\Pi_{\underline{D}}\right)}{\eta_{0}} + k\lambda \left(1 - \frac{\eta\left(\Pi_{\underline{D}}\right)}{\eta_{\infty}}\right) \underline{\underline{\sigma}} : \underline{\underline{D}}$$
(10)

When the viscosity function $\eta(II_{\underline{D}})$ tends to a constant, i.e., $\eta(II_{\underline{D}}) \rightarrow \eta_0 = \eta_{\infty}$. And the codeformational Maxwell derivative is linearized $\underline{\sigma} \rightarrow \partial_t \underline{\sigma}$, the BMP reduce to the Maxwell model as a particular case (viscoelastic regime).

6.1.2 Steady state of the BMP model

In the following, we consider the steady-state version of equations (9) and (10), namely.

$$\left(\frac{1+k\lambda\left(\frac{\eta_{0}}{\eta_{\infty}}\right)\underline{\sigma}:\underline{D}}{1+k\lambda\underline{\sigma}:\underline{D}}}{1+k\lambda\underline{\sigma}:\underline{D}}\right)\underline{\sigma}+\frac{\eta_{0}}{G_{0}}\underline{\sigma}=2\eta_{0}\underline{D};$$
(11)

where the time derivative of the stress are set to zero in Eq. (9), i.e., $\partial_i \underline{\sigma} = \underline{0}$. The left hand of equation is a structural parameter, which may be considered as a measure of flow-induced departures of structure from a reference state. Here, the reference state is defined as the viscosity at vanishing shear rate η_0 . Equation (11) contains four property materials: (i) two viscosities to low and high shear rate η_0 , η_{∞} , (ii) relaxation structural time λ , (iii) elastic modulus G_0 and one fitting numerical parameter k that can be interpreted physically as a kinetic constant for the structure break-down. It is important to note that equation (11) is quadratic in the stress and embodies particular cases discussed elsewhere. [Bautista et al. 1999, Manero et al. 2002].

The BMP model was selected for this study due to its capacity of predicting the thixotropic behavior of structured fluids such as: (i) worm-like micellar solutions, (ii) dispersions of lamellar liquid crystals, (iii) associative polymers, (iv) bentonite suspensions, (vi) polymer like micellar solutions and (vii) nanocomposites. In addition, the model reproducing the complete flow curve for a shear thinning and shear-thickening fluid, i.e. a Newtonian plateau at low and high shear rates, an intermediate power- law region and non-vanishing normal- stress differences; it also gives a reasonable description of the elogational and complex viscosity with finite asymptotic value and mono-exponential relaxation stress relaxation and start-up curves, thixotropy and shear banding flow [Soltero et al. 1999; Bautista et al. 1999; 2000; 2002, Manero et al. 2002, Escalante et al. 2003, Escalante et al. 2007; Calderas et al. 2009].

Analytical solutions for the simple shear flow are obtained by using this model due to its simplicity as compared to more complex models [Acierno et al. 1976; De Kee et al. 1994; Giesekus 1966, 1982, 1984, 1985, Quemada et al. 2003]. Furthermore, all five parameter of the model are related to the fluid properties and can be estimated from rheological experiments in steady and unsteady state as described elsewhere [Bautista et al. 1999]. The viscosities η_0 and η_{∞} can be obtained from low and high-shear-rate plateau in steady shear measurements. G_0 can be obtained by oscillatory shear measurements or from instantaneous stress relaxation experiments. The agreement between the values of G_0 obtained from these two experiments is within 10%[Soltero et al. 1996]. The structural relaxation time λ can be estimated from the intercept of the stress relaxation times at long times alter cessation of steady shear flow, where the intercept is given by $Exp[-G_0\lambda(\eta_{ss}^{-1} - \eta_0^{-1})]$, being η_{ss}^{-1} the steady state fluidity (inverse of the viscosity) prior to the cessation of shear flow. The parameter k, in turn, can be evaluated from the stress growth coefficient η^+ from inception of shear flow experiments [Soltero et al. 1999].

6.2 Lineal viscoelastic regime 6.2.1 Multi-modal Maxwell equation

In the case, when the system has a constant structure, the structure parameter and the dimensionless number goes to the unit, i.e., $\xi(II_{\underline{D}}) = B_i \rightarrow 1$ the multimodal version of the BMP (Bautista-Manero-Puig) model reduces to the multimodal version of the codeformational Maxwell equation [Bautista et al. 1999, Manero et al. 2002].

$$\underline{\underline{\sigma}} = \sum_{i=1}^{N} \underline{\underline{\sigma}}_{i}$$
(11)

$$\underbrace{\sigma}_{=i} + \lambda_{0i} \underbrace{\sigma}_{=i} = 2\lambda_{0i} G_{0i} \underbrace{D}_{i}$$
(12)

In the lineal viscoelastic regime, equations (11, 12) reduces to the Maxwell model, and the well-known storage and loss modules of the Maxwell Model [Bautista et al. 1999, Manero et al. 2002].

$$G''(\omega) = \sum_{i=1}^{N} G_{0i} \frac{(\omega \lambda_{0i})^2}{1 + (\omega_0 \lambda_i)^2}$$
(13)

$$G'(\omega) = \sum_{i=1}^{N} G_{0i} \frac{\omega \lambda_{0i}}{1 + (\omega \lambda_{0i})^2}$$
(14)

 G_{0i} and λ_{0i} , represent characteristic values of moduli and the corresponding relaxation time, respectively. The parameters G_{0i} and λ_{0i} of each sample were calculated using nonlinear regression data of the corresponding oscillatory flow curves G '(ω) and G'' (ω) [Calderas et al. 2009]

6.3 Rheometry

In this section, results for the nanocomposites PET-PEN/MMT clay studied under steady shear, instantaneous stress relaxation and relaxation after cessation of steady shear flow are reported.

6.3.1 Steady shear flow experiments

6.3.1.1 PET-PEN blend

Rheological measurements have been reported for the pure PET and PEN polymers as well as for PET-PEN blends at 270°C using a TA-Instruments AR 1000-N controlled stress rheometer with parallel plates of 25 mm diameter and 0.75 mm gap [Sánchez-Solís et al. 2005a]. The low shear rate viscosity of PEN is about ten times that of PET, and the shearthinning region of the former starts at 2 s⁻¹ while that of PET begins at higher shear rates (around 20 s⁻¹). Shear viscosities of PET-PEN blends processed at 270°C with 2 min residence time tend to a plateau at low shear rates and shear thinning for shear rates larger than 10 s⁻¹. The low shear- rate viscosity was found to increase in a direct relation to PEN content in the blend at 270°C with 2 min residence time. It is important to mention that the extent of transesterification reaction and %transesterification reached the highest values for these conditions. The effect of the extruder processing temperature on the blend was also reported; temperatures at the extruder exit die of 270, 280 and 290°C were applied. Agreement between first Newtonian viscosity and %transesterification was found for the conditions studied.

6.3.1.2 PET-MMT nanocomposite

With respect to PET-MMT nanocomposites, viscosity at low shear rate using the same rheometer have been measured [Sánchez-Solís et al. 2003]. All measures were reported at 270 °C with samples having the same thermomechanical history. The effect of clay content and additives (MAH and PENTA) was studied. It was found that the low shear viscosity (zero shear viscosity) decreased with clay content to values less than half those of PET for 2% clay content. Additives were found to reduce viscosity at 2% clay content even more, but they show no effect at lower clay contents. The effect of diminishing viscosity with clay content (in the 1-2% range) is an important issue to consider. Cost reduction due to the energy savings to process the nanocomposite and better filling of the mold cavities, etc., are some benefits. However, the effect is far from being totally understood, but from what has been discussed in this chapter so far, the difference in nanoparticle concentration in the surface as compared to the bulk nanocomposite (see section 2), as well as the formation of a slip layer (see section 5) may be the key issues to explain this effect.

To address the effect of clay modified with different additives (MAH, PENTA and the alkylammonium chlorides, see section 4.2 for details) [Sánchez-Solís et al. 2004] three different PET samples were studied: pellets of PET as received, PET extrudedonce, and PET extruded and mold-injected. It was shown that while the decrease in the viscosity due to extrusion is relatively small (from 400 to 300 Pa s). The large drop observed in molded samples is quite drastic (from 300 to 30- 40 Pa s). This extremely large decrease in the shear viscosity of the molded samples is also accompanied with a strong decrease in the viscousmodulus of almost a decade as measured in linear viscoelastic oscillatory tests (as will be discussed in the oscillatory flow section). Again it was demonstrated that the shear

viscosity of the PET-MMT nanocomposites decreased with clay content (up to 2%) as compared to PET extruded once. Newtonian plateau was found to extent to higher shear rates (onset of shear thinning) with clay content (no additives). Nanocomposites with additives (MAH and PENTA) showed similar trends in viscosity as compared to systems with no additives, which lead to the conclusions that the main effect in viscosity changes was attributable to the nanoparticles alone. The rheological properties for the 1% and 2% clay (nDodecylammonium) systems were also reported. Molecular weight was found to diminish with the addition of modified clay (nDodecylammonium) and while the viscosity of the 1% modified clay (exfoliated) system showed a similar viscosity curve as extruded PET (constant viscosity in almost all the shear rate range studied) but with lower viscosity values, the 2% modified clay system (non exfoliated) exhibits a loss of Newtonian plateau and lower values of viscosity throughout the range studied.

6.3.1.3 PET-PEN-MMT nanocomposite

As expected from previous results, a decrease in the shear viscosity upon clay addition was found in the PET-PEN-MMT clay nanocomposites [Sánchez-Solís et al. 2005b]. The clay-Na+ blend presented a slightly larger zero shear viscosity than the other blends (clay-MAH and clay-C18), but the onset for shear-thinning is similar to that of the precursor polymers PEN and PET.

The steady-state shear viscosity for the pure PET-PEN polymer matrix has been compared to that of a PET 80%- PEN 20% - 1% MMT organically modified clay nanocomposite (quaternarium ammonium salt modified clay), after processing the matrix at the same conditions used to process the nanocomposites. For this clay nanocomposite the zero shear viscosity is lower than that of the unfilled matrix [Calderas et al. 2009]. This behavior is in agreement with that of the previous discussion.

6.3.2 Oscillatory flow

6.3.2.1 PET-PEN blend

For the PET-PEN blend, a high degree of correlation between the storage modulus, G' (as measured in linear viscoelastic regime), the % transesterification and the steady state shear viscosity was found. To study compatibility between PET and PEN polymers, master curves of G' versus G'' were prepared. A good correlation was found at the three temperatures (270, 280 and 290 °C) and two extruder residence times (2 and 4 min) except in the low frequency region. Slopes lower than two in the low frequency region of the elastic modulus were associated to the presence of an elastic network.

These results suggest that the same degree of compatibility is found at all processing conditions studied and this was verified with Tg measurements, revealing only one Tg for all blends.

6.3.2.2 PET-MMT nanocomposite

Complex viscosity (measured in the linear viscoelastic region) was found to decrease with clay content in a similar fashion as steady state shear viscosity (as mentioned in section 6.3.1.2) for PET-MMT nanocomposites. However, decreasing viscosity with frequency was not observed as opposed to the shear viscosity. This result leads to the conclusion that continuous shear caused particle flow alignment with the consequent shear thinning

behavior. Storage modulus (G') was measured, and a decrease of viscoelastic properties with clay addition was observed, in agreement with continuous shear viscosity. The presence of nanoparticles was evidenced in the low frequency region with a G' slope change (deviation from the Maxwell slope value of 2). This is an evidence of solid-like behavior (frequency independent G') in these systems.

As was previously mentioned (section 6.3.1.2) a large decrease in viscosity and storage modulus G' was observed for pure PET when the sample was mold-injected. This is directly related to a molecular weight loss (measured and reported). Storage modulus was found to increase in the exfoliated samples surpassing the G' values of extruded PET. This effect was shown to be independent of molecular weight changes and was attributed to the nano-particles only. In the nanocomposites, the values of the G' showed no direct relation to sample molecular weight, i.e., one non-exfoliated sample with one of the lowest molecular weight reached G' values higher than those of extruded PET, which was attributed to a high degree of particle dispersion in the PET matrix.

6.3.2.3 PET-PEN-MMT nanocomposite

For the PET-PEN-MMT nanocomposite, a solid-like response was reported for the unmodified clay (clay-Na⁺) and Octadecylammonium modified clay (clay-C18) [Sánchez-Solís et al. 2005b]. Such behavior was ascribed to larger particle–polymer interactions, which lead to a larger number of molecular entanglements in the blend.

This strong polymer-nanoparticle interaction was studied in a PET-PEN-organically modified MMT in detail by performing instantaneous stress relaxation, relaxation after cessation of flow and start-up rheological test [Calderas et al. 2009]. Results are discussed in the following sections.

6.3.3 Instantaneous stress relaxation

In this test, an initial small-amplitude strain is applied to the sample during a period t1 (which depends on the apparatus used). This period in the present case is 0.06 s. Then, for all t > t1, the stress is allowed to relax. The stress relaxation modulus G(t), i.e., the shear stress divided by the applied strain, is plotted versus time. The stress was monitored until a terminal slope was reached. The time necessary to reach the terminal slope was found to be about 60 s for all materials. All systems showed two main modes of relaxation times (λ), a slow mode associated to the initial slope (short times) and a fast one associated to the final slope (longer times).

As expected, pure PEN (largest steady shear viscosity) possesses the highest initial modulus (around 600 Pa), but the transition between the two main modes of relaxation is smoother as compared to the other systems. The sharpest shift between the two main modes is observed to occur in pure PET, while for the PET-PET blend and for the nanocomposite, the shift is not as sharp as for pure PET, nor as smooth as for pure PEN.

Normalized relaxation curves (with initial G(t) value) for three systems were analyzed in a log-log plot. PET showed a rapid and more pronounced initial relaxation, while in the other systems (PET-PEN and PET-PEN-clay) the presence of PEN and the clay somehow restricts the rapid relaxation and there is a rapid change towards the slow mode which is evidenced by an earlier change of slope. The response at long times for the instantaneous stress relaxation curve has been associated to the polymer-filler interactions. For these systems the

terminal slope is similar for the pure PEN and for the nanocomposites system. In the case of the polymer blend, PET and PEN chains form a network promoted by the transesterification reaction that occurs at the processing conditions, which produces a copolymer and mutual crosslinking. For the nanocomposites, the relaxation is also restricted but the presence of the clay induces different dynamics. In this case, the relaxation is not as slow as for the polymer blend, (this is clearly observed in the large slope at long times) possibly caused by a particular polymer-clay interactions, since the high molecular weight chains are absorbed preferentially in the clay galleries, thus allowing more mobility in the nonabsorbed low-molecular weight chains. In addition, it has been reported that in the presence of the clay in the polymer matrix somehow restricts the amount of cross-linking and thus the copolymer formation (see discussion at the end of section 1).

A Fourier Transform (FT) frequency response was obtained from the relaxation curves and compared to the linear oscillatory data. A good agreement was found between both viscoelastic data.

The results were modeled by the above exposed rheological equation of state [see section 6.1]. The model was used to find the characteristic times of the slow and fast modes for the systems. The model for pure PEN requires 3 relaxations times or modes, pure PET and the PET-PEN blend require 4 relaxation times and the nanocomposites requires 5 modes, revealing the complexity added by the presence of the clay. The two main modes for the systems are disclosed in Table 3. Comparatively, the characteristic time of the slow mode in the PET-PEN systems is the largest, reflected in the plateau of the relaxation curve and related to the effect induced by the transesterification reaction occurring in the system which produces an amount of cross-linking [Calderas et al. 2009]. The characteristic times of the fast modes have similar values.

6.3.4 Start-up of shear flow

Stress growth was reported as a function of time showing that the material with added clay reaches the maximum stress. This maximum value reflects the initial elasticity of the system, evidencing the formation of an elastic network induced by strong polymer-matrix interactions in the nanocomposite. Curves for PET and PET-PEN blend overlap, showing no significant change. The amplitude of the overshoots has been proposed to be related to the degree of exfoliation of the nanoclays. Furthermore, overshoots in polymer-clay systems have been attributed to the break-down of a clay platelet network [Calderas et al. 2009].

6.3.5 Relaxation after cessation of steady state flow

In this experiment, the sample is sheared at constant and steady shear rate (10 s⁻¹). At time t = 0, the flow is suddenly stopped and the relaxation of the stress is followed as a function of time. PET was reported to show a fast relaxation, while PET-PEN and PET-PEN-MMT display a similar slope at long times. The behavior at long times reflects chain cross-linking in the case of PET-PEN blend and a polymer-clay interactions in the case of the nanocomposites.

Table 4 shows the values of the two main relaxation times for the samples. With exception of PEN, all curves display similar initial fast relaxation time. At long times, PET shows a fast decay to very slow value of stress, i.e., below the rheometer resolution. The relaxation curve for the PET-PEN system seems to stabilize at long times and presents the largest

characteristic times of the slow mode (see Table 4). This may be attributed again to the crosslinking induced by the reaction among the polymers, while the PET-PEN-clay blend shows a small relaxation time of the slow mode. This system is thought to have experienced a structural break up due to the constant shear flow imposed before the relaxation dynamics and thus the system becomes less structured (possibly flow alignment of clay nanoparticles) affecting the relaxation dynamics after flow cessation.

Modes	PEN	PET	PET-PEN	PET-PEN/MMT
Slow	6.83	11.95	13.82	6.50
Fast	0.12	0.10	0.13	0.09

Table 3. Main Relation times $\lambda[s]$ for the materials as obtained from instantaneous stress relaxation data

Modes	PEN	PET	PET-PEN	PET-PEN/MMT
Slow	1.24	0.312	1.74	1.50
Fast	0.10	0.017	0.016	0.016

Table 4. Main relaxation time $\lambda[s]$ obtained from stress relaxation after cessation of steady shear

7. Conclusions

A comprehensive review on the preparation by melt extrusion and characterization of PET-MMT and PET-PEN-MMT nanocomposites was presented. Emphasis was made in presenting results related to the mechanical properties, morphology and flow characteristics of nanocomposites using different experimental techniques. The influence of several factors such as processing conditions, clay modification, clay content, %transesterification and compatibilizing additives was discussed and analyzed. Several important issues arise from the analysis of these systems, i.e. there is a decrease in shear viscosity with clay addition which still is far from being totally understood. However this effect can be beneficial to processing, reducing energy necessary to melt compounding and injecting and filling mold cavities. Nevertheless, special care has to be taken in order to reduce sample sagging during processing due to small viscosity, and hence temperature profiles will have to be adjusted accordingly. The formation of a slip layer in the surface of flowing samples and the migration of nanoparticles away from the surface seem to be key issues to explain the viscosity reduction effect, even though other factors such as slippage at particle-polymer interphase, particle alignment, particle migration and polymer absorption in the particles will have to be studied to fully understand this effect. Solid-like behavior is another important effect and it seems to be strongly associated to polymer-particle interaction. Final, it still not clear if clay exfoliation, clay modification or clay addition are sufficient conditions to obtain high performance nanocomposites and further investigation will be required to understand and finally produce adequate nanocomposites for specific applications.

8. References

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Synthesis of Nanosized Luminescent Materials and Their Photoluminescence under VUV Excitation

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1. Introduction

Photoluminescence (PL) phosphor can be divided into different types according to the different excitation wavelengths, and they have different applications. The region from 100 to 200 nm is the vacuum ultraviolet (VUV) region and the phosphors excited by VUV light are usually used for plasma display panels (PDPs) and Hg-free lamps.¹ Nowadays, the PDP and liquid-crystal displays (LCDs) are the two most widely used techniques in flat panel display technology. Comparing with LCD, PDP display technique could provide rapider response of pictures, higher contrast and larger viewing angle.² Hence, PDP is a promising candidate for the large flat-display industry, especially in 3D displays.

Although PDP are currently available commercially, there are several disadvantages which limited its further application. First of all, PDP has lower luminescent efficiency (Tab. 1). Comparing with several common luminescence techniques, the luminescent efficiency of PDP is lowest.³

luminescence techniques	luminescent efficiency (lm/W)
Fluorescent lamp	80~100
cathode ray tube (CRT)	5~6
LCD	2~3.5
PDP	1~1.5

Table 1. Luminescence efficiency of several luminescence techniques.

VUV commercial phosphor	Applied deficiency	Influences on display
(Y,Gd)BO3:Eu3+	Low color purity (0.641, 0.356)	poor color purity
BaMgAl10O ₁₇ :Eu ²⁺	Low thermal stability (Intensity decrease >15% under 500 °C,10 h)	Shorten useful life
Zn ₂ SiO ₄ :Mn ²⁺	Long decay time (14.23 ms)	Image delay

Table 2. Main deficiencies of tricolor commercial phosphors for PDP.

Secondly, the representative tricolor commercial phosphors for PDP were (Y, Gd)BO₃: Eu³⁺, ZnSiO₄:Mn²⁺ and BaMgAl₁₀O₁₇: Eu²⁺ (BAM). However, there are still some deficiencies in these phosphors: The color purity (Y, Gd)BO₃:Eu³⁺ was poor and the decay time of ZnSiO₄:Mn²⁺ was too long for the application, while the instability of BaMgAl10O17:Eu2+ under VUV radiation and thermal treatment was an outstanding problem during panel manufacture (Tab. 2).⁴

What is more, the mechanism of VUV excited luminescence is not clear. The ultraviolet (UV) excited phosphor is usually originated from direct excitation activators. However, the luminescence process under VUV excitation is only considered as the host transfer absorbed excitation energy to activators (Fig. 1).⁵ The Specific emission process is not clear. So current research about VUV phosphor focus on these aspects: Improvement on traditional phosphors, development of new phosphors and investigation of luminescence mechanism.



Fig. 1. The luminescence mechanism under UV/VUV excitation.

Recently, many researchers have focused on the preparation and luminescent properties of nano-phosphors because of their different characteristics compared to those of their bulk counterparts. As particles diameter approaches to their Bohr diameter, the optical properties begin to change and quantum confinement effect begins to play a much more important role. It results in great differences in physical and electronic properties between the nanometer-scale particles and bulk materials. Besides, to meet the requirement of the PDP manufacture procedure, nanophosphors were convenient to brush the panel and they could get higher resolution to make the pictures more vivid.^{6,7} However, due to restriction on the test equipment, much research about nanophosphors were limited to investigating their optical properties in the UV region. And the optical properties of nanophosphors under VUV excitation.

With the expectation of improving the physical, chemical and luminescent properties of ordinary phosphor particles, many soft-chemical techniques have been adopted to synthesize nano-particles on the account of their good mixing of starting materials and relatively low reaction temperature.⁸⁻¹⁰ In this work, the nano-scaled tricolor phosphors: YBO₃:Eu³⁺, ZnSiO₄:Mn²⁺ and BaMgAl₁₀O₁₇:Eu²⁺, and other VUV excited phosphors were respectively prepared by different soft-chemical methods, such as solvent-thermal, hydrothermal method and sol-gel process. Our works focus on controlling the size and morphology, improving PL performance and investigating special properties of nanophosphor under VUV excitation. All data in this chapter have been published and all contents are contained in these papers (from ref. 11 to 18).¹¹⁻¹⁸

2. Red phosohor of YBO₃:Eu³⁺

YBO₃:Eu³⁺ is a promising red phosphor owing to its high ultraviolet (UV) and VUV transparency, non-linear properties and exceptional optical damage threshold which allows it to withstand the harsh conditions presenting in vacuum discharge lamps or screens.¹⁹ In particular, it exhibits extraordinarily high luminescent efficiency under VUV excitation. However, all of these advantages do not make YBO₃:Eu³⁺ as a desired VUV phosphor because of its poor chromaticity. In the emission spectra of YBO₃:Eu³⁺, the main emission are composed of two transitions: a typical magnetic dipole transition ⁵D₀–⁷F₁ (orange color), and a typical electric dipole transition ⁵D₀–⁷F₂ (red color). It is well known that the ⁵D₀–⁷F₂ transition is hypersensitive to the symmetry of the local crystal fields surrounding the Eu³⁺ ions. When Eu³⁺ ions occupy the inversion sites, according to the selective rule, the magnetic dipole transition is permitted but the electric dipole transition is forbidden, and then causes a poor chromaticity, which is to say that the color purity of the YBO₃:Eu³⁺ would improve by decreasing the particle size of the YBO₃:Eu³⁺ phosphor.^{20,21}

2.1 Controllable morphology of YBO₃:Eu³⁺ nanophosphors

Reports about preparing various morphologies and sizes of YBO₃:Eu³⁺ are scarce. Because the natural growing habit of YBO₃ is sheet-like,²²⁻²⁴ which always plays an important role in determining the final morphology of YBO₃:Eu³⁺. In addition, YBO₃:Eu³⁺ are apt to form highly agglomerated particles²⁵ and it is the "thermodynamic-stable species" that could only be obtained under harsh conditions, so no efficient control over their size and morphology has been achieved yet.²⁴ Many works have been reported for preparing the different morphology and size of YBO₃:Eu³⁺ nanophosphor.^{20,24,26-28} However, there is no report about preparing various morphologies and sizes of YBO₃:Eu³⁺ only by adjusting one reaction condition in one simple method. In this paper, we first prepared multifarious morphologies and sizes of YBO₃:Eu³⁺ by adjusting the pH value of precursors in hydrothermal reaction (HR) method at a low temperature of 260 1C for 3 h, in the absence of any surfactant and template, without milling and post calcination. The relationships between pH value of precursors and samples' morphologies, sizes, were discussed.

Samples pH	Mean grain size (nm)
6	25.1
7	19.1
8	17.7
9	23.5
9.5	68.2
10	238.2
11.28	475.0

Table 3. Mean grain sizes of samples.

As shown in Fig. 2, most diffraction peaks of HR samples display a broadening behavior and quite different intensities compared with those of Solid state Reaction (SR) sample. It indicates that the morphologies and sizes of HR samples have great changes. The particle size can be estimated from the Sherrer equation. The calculated mean grain sizes are listed in Tab. 3. It should be stated that the Sherrer equation is tenable when the grain size is less than 100 nm. Hence, the calculated values which are more than 100nm can only be employed to do qualitative analysis. With the pH values of precursors going on increasing, the mean grain sizes increase dramatically. For sample 9.5, the size increases to 68.2 nm. Samples 10 and 11.28 are no longer in nanoscales.



Fig. 2. XRD patterns of all YBO3:Eu0.05 samples

Fig. 3a shows the typical TEM image. The particles are irregular sheet-like and decrease to nano-sized. Their thicknesses are estimated to 20–40nm and the planar sizes are distributed in the range 40–120 nm. The typical FE-SEM images of sample 6 are exhibited in Fig. 3b and c. The sheet-like nano-particles are clearly observed. Fig. 4a exhibits the typical TEM image of sample 7. These particles are similar to those of sample 6. However, the typical FE-SEM images (Fig. 4b and c) clearly show that these small nano-sheets are apt to connect each other in one layer to form some bigger nano-sheets, whose thickness are still nano-size but planar sizes can reach to microsize.

Fig. 5 displays the typical TEM image and FE-SEM images of sample 8. In this sample, the aforementioned bigger nano-sheets assemble more tightly that make clusters like blooming flowers and downy balls. Most clusters are about 6–8 mm. Fig. 6a exhibits the typical TEM image of sample 9. The nano-sheets show stronger tendency to agglomerate with each other. Correspondingly, it can be clearly observed in the FE-SEM image (Fig. 6b) that all the nano-sheets assemble to form blooming flower-like clusters with sizes about 4–5 mm, which are somewhat smaller than those of sample 8.



Fig. 3 (above). and 4 (botom). Electron microscopy images of $YBO_3:Eu_{0.05}$ sample prepared by HR method with precursor pH=6 (sample 6, Fig. 3) and 7(sample 7, Fig. 4). (a) TEM and SAED images. (b,c) FE-SEM images.



Fig. 5 (above). and 6 (botom). Electron microscopy images of YBO₃:Eu_{0.05} sample prepared by HR method with precursor pH=8 (sample 8, Fig. 5) and pH=9 (sample 9, Fig. 6). (a) TEM and SAED images. (b,c) FE-SEM images.

As shown in Fig. 7, particles' morphology and size change dramatically for sample 9.5. Some particles change to rod-like whose diameters are distributed in the range 200–1500nm and the lengths are about 5–20 mm, others grow into bigger sheets with planar sizes about 3–20 mm. With precursor pH value increasing to 10, more rod-like particles form (Fig. 8). At the same time, the sheets still exist in the products, and their planar sizes increase to 5–30

mm. The aspect ratios of most rods are higher than those of sample 9.5, for their lengths increase to 10–50 mm range but diameters change little.



Fig. 7 (above). and 8 (botom). Electron microscopy images of $YBO_3:Eu_{0.05}$ sample prepared by HR method with precursor pH=9.5 (sample 9.5, Fig. 7) and pH=10 (sample 10, Fig. 8). (a) TEM and SAED images. (b–e) FE-SEM images.

When the pH value of precursor increases to 11.28, which is the highest value that can be adjusted in our experiment, the morphologies and sizes of the particles change dramatically once more as Fig. 9 shown. The rod-like particles are replaced by lots of uniform, non-aggregated, quasi-spherical, nano-sized particles with the diameters about 20–30 nm. Some nano-sheets still exist in this sample. Both sheet-like and quasi-spherical particles are monocrystallines.



Fig. 9. Electron microscopy images of YBO₃:Eu_{0.05} sample prepared with precursor pH=11.28 (sample 11.28). (a) TEM and SAED images. (b,c) FE-SEM images.

In conclusion, the XRD, TEM and SEM give the accordant result about the morphologies and sizes of all samples. For HR samples, the particles' morphologies and sizes intensively depend on the pH value of the precursors, and particles have a tendency to form monocrystallines with increasing the pH.



Fig. 10. (a) Emission spectra of all YBO₃: Eu_{0.05} samples; (b) R/O of all YBO₃: Eu_{0.05} samples

All samples were investigated their PL properties under 147nm excitation and the emission spectra was showed in Fig. 10. All spectra in Fig. 10 consists of sharp lines ranging from 580 to 700 nm, which are associated with the transitions from the excited ${}^{5}D_{0}$ level to ${}^{7}F_{I}$ (J=1, 2, 3, 4) levels of Eu³⁺ activators.^{29,30} The major emissions of YBO₃:Eu³⁺ is at 592 nm ($^{5}D_{0} \rightarrow ^{7}F_{1}$) and 611 and 627 nm (${}^{5}D_{0} \rightarrow {}^{7}F_{2}$), which correspond to orange and red color, respectively. It is well known that the relative intensity of ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ transition (orange light) or ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ transition (red light) depends strongly on the local symmetry of Eu³⁺ ions. When Eu³⁺ ions occupy the inversion center sites, the ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ transition should be relatively strong and when Eu³⁺ ions occupy the lower symmetry site, the ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ should be relatively strong.²⁰ As seen in the emission spectrum of SR samples, the peak at 592 nm is dominant. Whereas in our hydrothermal samples, the ${}^{5}D_{0} \rightarrow 7F_{2}$ transition located at 611 nm is strongest. The emission intensity at 611 nm increase as pH value, and reach to the strongest when pH=9. It indicates better color purity. The color purity of Eu³⁺ doping phosphors can be characterized as the intensity ratio between the red emission (${}^{5}D_{0} \rightarrow {}^{7}F_{2}$) and the orange emission (${}^{5}D_{0} \rightarrow {}^{7}F_{1}$) (R/O ratio). The R/O ratios of these samples are shown in Fig. 10b. It can be seen the nanosized YBO3:Eu3+ have higher R/O ration than bulk samples (SR). When PH=9, the emission intensity and (R/O) ratio reach to the highest.

2.2 Improvement PL performance of YBO₃:Eu³⁺ nanophosphors

From above section, we got the different size and morphology of nanosized YBO₃:Eu³⁺ by adjusting the PH value. What is more, the PL properties could also be adjusted. However, the nanophosphor has relatively lower luminescence intensity comparing with their bulk counterparts, which is due to milder synthesis condition leading to the nanopaticles with lower crystallinity and high surface defects density. So the further thermal treatment is needed to increase the PL intensity. However, nanophosphors usually would agglomerate after thermal treatment, which means that the morphology was broken and the particle size growth up. For YBO₃:Eu³⁺, the color purity would decrease as particle size growth up.



Fig. 11. XRD patterns of the YBO₃:Eu³⁺samples prepared with different ratios of water to solvent

On the other hand, the ideal phosphor would have the smaller size, high luminescence intensity, good color purity and well dispersion. In order to reach these purposes, some solvent was added during the reaction process. It used to control the particle size during the reaction process and keep the morphology during the heat treatment.

Fig. 11 shows XRD patterns of the samples synthesized with different ratios of water to solvent. All the diffraction peaks could be indexed to the JCPDF card (No. 83-1205), and there is no second phase observed. As shown in the Fig.11, the relative intensity of the diffraction peaks for the solvent-thermal (SO) samples are different from the sample prepared by hydrothermal reaction (HR, the 1:0 samples). The (002) peak is the strongest for the HR samples but the (100) peak becomes strongest when the solvent was introduced in the reaction systems, indicating the appearance of a preferred orientation.

The TEM photographs of the SO and HR samples are shown in Fig. 12. In Fig. 12a, we could find that the HR particles are rod-like with size of 150nm in diameter and 300nm in length. By the addition of solvent, the morphology changes into nano-sheets and the size is less than 50 nm. The particles in SO sample also represents better dispersion than that of HR samples. The morphology change here is consistent with the change of preferred orientation in XRD patterns. This result indicates that adding solvent will be conducive to decrease grain size and improve dispersion of the sample particle. It is accepted that nanoparticles crystallized by the dissolution-reprecipitation mechanism during the hydrothermal reaction,³¹ and this mechanism is also suitable for our system. Solvent and water present different physical properties. With the addition of solvent to the aqueous solution, the dielectric constant of the mixed solvent decreased, and led to the decrease in solubility of the reaction materials during the crystallization process. As a result, this led to the formation of smaller particles.³²



Fig. 12. The TEM images of YBO3: Eu3+ phosphors prepared by different reation. (a) HR Samples; (b) SO samples

Under 147nm excitation, the emission spectra of the SO samples with different ratios of water to solvent are shown in Fig. 13. It is observed that the strongest red emission is at the water to solvent ratio of 1:2, and the PL intensity of 1:3 samples is lower obviously than the others. It can be due to the existence of a small amount of OH⁻ coordinated to lanthanide ions at the surface of phosphors prepared by the wet chemical method. Adding excessive amount organic solvent (over 1:3) lead to large number of OH⁻ adhering on the surface of phosphor, which result in the poor PL intensity.³³ As can be seen in the figure, the ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ emission increased and ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ emission decreased with solvent added. This must be associated with particle size of samples (observed before). It is well known that the relative intensity of ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ transition ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ transition depends strongly on the local symmetry
of Eu³⁺. When the particle size decreases, smaller particles have more effective surface area and more lattice distortion, leading to many Eu³⁺ ions occupying lower symmetry sites. This will increase the transition probability of ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ and thus improve color purity.²⁰ It was found that the ratio of red emission (611nm) intensity to orange emission (592nm) intensity (R/O) is 1.11 for the 1:2 sample, which is the highest value among above samples. It predicts that the SO sample (solvent at 1:2) has the best color purity. The R/O ratios, chromaticity coordinates and relative luminescence intensity under VUV excited of the optimum samples were listed in Tab.4. As seen, the optimum nanophosphor sample has a better R/O ration and chromaticity coordinates is better than bulk and commercial red phosphor KX-504A. Meanwhile, the relative intensity was close to the bulk phosphor.



Fig. 13. Emission spectra of YBO₃:Eu³⁺ nano-phosphors prepared at different ratios of water to solvent. (a) 1:0; (b) 1:1; (c) 1:2; (d) 1:3 (λ_{ex} =147nm)

	R/O	Х	Y	Ι%
		(λ _{ex} =1	47nm)	-
NTSC		0.67	033	
KX504	0.69	0.644	0.355	100%
bulk	0.66	0.641	0.358	81.15%
Optimum sample	1.10	0.645	0.354	78.83%

Table 4. The R/O ratios and Chromaticity coordinates of the nano sample and bulk sample

2.3 Unique PL properties of YBO₃:Eu³⁺ nanophosphors under VUV excitation

In the above section, we got the YBO₃:Eu³⁺ nanophosphor with controllable morphology and size, and its PL performance was also improved. Meanwhile, as the nanophosphor, it should have many unique PL properties under VUV excitation comparing with bulk phosphor. A phosphor under VUV excitation has different PL mechanism comparing with that under UV excitation. This will be possible to generate some novel phenomena in nanophosphors. Here, we adopt a low temperature hydrothermal method without further treatment process to obtain YBO₃:Eu³⁺ nanophosphors. With controlling the reaction times, we got the $YBO_3:Eu^{3+}$ nanophosphors with different grain size. Through compare the different between UV and VUV spectra, we initially obtain the unique PL phenomenon under VUV excitation.

Fig. 14 shows XRD patterns of YBO₃:Eu³⁺ samples synthesized with hydrothermal reaction (HR) for different times. All samples were well-crystallized, and they could all be recognized as single phase in terms with JCPDF (83-1205). No second phase was observed. The relative intensities of different peaks changed with holding times. The intensity ratio of (100) to (102) increased as time increased from 3 to 9 h. The (100) peak, usually the strongest in these samples, became the third strongest in the 9 h samples. When the holding time was extended from 9 to 15 h, the (100) peak became the strongest again. The intensity ratio between other peaks, such as (002) to (100) and (110) to (104), also changed with extended time. This shows that the preferred orientation has been changed. By using the Scherrer formula to calculate grain size from each diffraction peak of the samples reached nanoscale, and the grain sizes did not change significantly with increased holding time (24.99–26.59 nm). This suggests that we could get nanosized YBO₃:Eu³⁺ phosphor lasting only 3 h. With increasing holding time, the crystallinity and grain size do not transform obviously, but the preferred orientations change.

Samples	average grain size (nm)
3h	26.03
6h	26.06
9h	25.76
12h	26.59
15h	24.99
SR	>100

Table 5. Average grain size of HR samples



Fig. 14. XRD patterns of YBO₃:Eu³⁺ samples synthesized by different times.

The SEM photographs of the 3 and 9 h samples are shown in Fig. 15, and the TEM photographs are shown in Fig. 16. As can be seen in Fig. 15, the two samples consist of nanosheets, but the morphology and aggregation states are different. The nanosheets in the 3 h sample regularly aggregate into rose-like spherules, and the diameter of each spherule is about 2–3 μ m (Fig. 15a and c). In the 9 h samples, they loosely aggregate together without order (Fig. 15b and d). In the TEM photographs (Fig. 16), the size of particles in the 3 h sample is about 300 × 150 nm (Fig. 16a). This differs from calculated results from XRD, indicating that a particle in this sample is polycrystalline and consists of several monocrystalline particles (Fig. 16a). In the 9 h sample (Fig 16b), many particles are nanosheets approximately 50–100 nm long and much thinner. Linking with the SEM, we can find orderly morphology is formed in a shorter time (3 h), but this morphology is broken and the aggregation state is dispersed when the time is extended to 9 h. This indicates that a recrystallization process is likely to exist with holding time change, and it could explain the relative intensities of diffraction peaks changed in XRD section. From above results, we can consider the particle size gradually decreases in this period of time (3–9 h).



Fig. 15. SEM photographs of YBO₃:Eu³⁺; (a) and (c), 3h sample; (b) and (d) 9h sample.

The VUV excitation spectra of 3, 6, and 9 h samples are presented in Fig. 17. The excitation spectra consisted of several bands in the range of 120–260 nm. The bands in the region from 190 to 260 nm could be result from the overlapping of two bands. One is located at 222 nm and probably is related to an excitonic transition (ET) from the O2*p* state to the Y (4*d* + 5*s*) state.^{34,35} The second band occurring around 237nm is known to be a charge-transfer (CT) process, which is related to an electron from the O 2*p* state to Eu³⁺ 4*f* state.³⁶ In the region from 120 to

190 nm, two bands are overlapped. One is the BO₃ group absorption (BA) band (peak at about 145 nm) and the other is the Eu³⁺ 4f-5d transition band (peak at about 154 nm).⁵



Fig. 16. TEM photographs of YBO₃:Eu³⁺; (a) 3h sample; (b) 9h sample.



Fig. 17. VUV excitation spectra of YBO₃:Eu³⁺ from 3h to 9h.

As for the bulk and submicrosized YBO₃:Eu³⁺ samples, only one band could be observed in the region from 190 to 260 nm because the two bands are overlapped. However, in the nanosized YBO₃:Eu³⁺ sample, as can be seen in Fig. 17, a blueshift of the ET band and a redshift of the CT band could be observed, and as a result, these two bands separated and could be distinguished. The phenomena could be explained by quantum size effects.²¹ With increased holding time, the position of the ET band did not change, but the blueshift of CT band was observed. The phenomena could be explained by quantum size effects.³⁷ Furthermore, with the particle size decreased (from 3 h to 9 h), the intensity of the CT band became weaker, but the ET band did not change evidently. The same phenomenon was observed in Y_2O_3 :Eu³⁺ sample,³⁸ due to surface effects in the nanophosphor and the absorption properties of CT and ET bands. At the same time, the intensity of the BA band became stronger. This can be considered to be caused by particle decrease. As is universally known, UV light has a large penetration depth for phosphors (several microns) but VUV light has a small penetration depth (<100 nm).³⁹ Therefore, the BA process could only occur close to the surface of the phosphor. With the size decrease, more areas could be irradiated, and VUV transparency increased, leading to the increased BA process. For nanophosphor, the small penetration depth of VUV light is an important factor to affect the PL properties, which usually lead totally different PL performance between UV excitation and VUV excitation. We have discovered a unique phenomenon about nanophosphor, which could be explained by the "self-purification" effect in nanosystems. And we made further discuss about the relationship between penetration depth of VUV light and VUV PL performance of nanophosphors.⁴⁰



Fig. 18. Emission spectra of YBO₃:Eu³⁺ (λ_{ex} = 254 nm) (a) different time HR samples and SR sample, (b) schematic diagram of intensity change.



Fig. 19. Emission spectra of YBO₃:Eu³⁺ (λ_{ex} = 147 nm) (a) different time HR samples and SR sample, (b) schematic diagram of intensity change.

Figs. 18 and 19 show the emission spectra under 254 and 147 nm excitation. For nanoscale YBO₃:Eu³⁺ phosphors compared to bulk YBO₃:Eu³⁺, the ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ transition is usually

relatively stronger because smaller particles have more effective surface area and more lattice distortion, leading to many Eu³⁺ ions occupying lower symmetry sites.^{3, 4} Figs. 18b and. 19b show the change trend of relative emission intensity at 592 and 611 nm under UV and VUV excitation. Several interesting phenomenon should be noted. Under 254 nm excitation, the luminescence intensity of HR samples decreased first and increased later (Fig. 18a and b). However, the emission under VUV excitation increased first and decreased later (Fig. 19a and b). For instance, the 3 h sample and 15 h sample have the strongest intensity in the series samples under UV excitation, but under VUV excitation, they are almost the lowest. From XRD and electron microscopy results, we could consider that the particle sizes of the YBO₃:Eu³⁺ phosphor decrease and then increase from 3 to 15 h, owing to a recrystallization process. These results show that in a certain nanoscale, the luminescent intensity under VUV excitation would increase but under UV excitation would decrease as the size decreased.

3. Green phosphor of Zn₂SiO₄: Mn²⁺

Zn₂SiO₄: Mn²⁺ has been widely used as an efficient green phosphor in plasma display PDPs, CRT, field emission displays (FED), backlight of LCD and electroluminescence (EL) devices due to high luminescent efficiency and chemical stability.⁴¹⁻⁴⁴ As far as the synthesis processes concerned, this phosphor was usually prepared by the solid-state reaction method, which involves a pulverizing process and subsequent high-temperature firing, and the resulting Zn₂SiO₄: Mn²⁺ powder possess diameters of about 2 and 20 µm with irregular shape.45,46 Recently, for advancing display device technology, fine particle phosphors with smaller size and more uniform shape than those commercially available phosphors are in urgent need.⁴⁷⁻⁵⁰ It is of interest to prepare nanoscaled phosphor to improve the dispersion and luminescence properties.⁵¹ Additionally, nanoscaled phosphor materials offer the potential for preparing smoother films with higher packing densities than conventional micron-sized phosphors.^{1,45} Many new methods for the preparation of Zn₂SiO₄: Mn²⁺ has been proposed, including sol-gel,⁵² spray pyrolysis⁵³ and hydrothermal method.⁵⁴ Among these synthesis methods, hydrothermal processing has great advantages, such as low processing temperature at high pressure, better metal ions distribution and lower cost.55 Therefore, we synthesized Zn₂SiO₄: Mn²⁺ nanoscaled phosphor at a low temperature via hydrothermal route, and their PL properties under VUV excitation were evaluated.

3.1 Controllable morphology of Zn₂SiO₄: Mn²⁺ nanophosphors

Fig. 20 shows the XRD patterns of $Zn_2SiO_4:Mn^{2+}$ phosphors prepared at different temperatures for 4 hours. All the diffraction peaks can be indexed to pure hexagonal-structured Zn_2SiO_4 (JCPDS card No.37-1485). No obvious impurity phase was detected. The XRD result shows that pure hexagonal-structured Zn_2SiO_4 can be obtained at a low temperature of 140°C, which is lower than that of 220°C reported by Wan et al.⁵⁵ and much lower than using the conventional solid-state reaction method. The XRD pattern in Fig. 21 exhibits that samples heated for different time are almost pure phase of Zn_2SiO_4 . The crystal structure had no obvious change as the sample was heated from 1 to 8 hours at 220°C. The $Zn_4Si_2O_7(OH)_2H_2O$ is not detected as reported by the Ref.,⁵⁶ which means that there is no intermediate phase in our hydrothermal procedure. The average crystallite sizes estimated from the Scherrer equation indicated all the samples were in nanoscaled.



Fig. 20. XRD patterns of the Zn₂SiO₄: Mn²⁺ samples prepared at different temperatures.



Fig. 21. XRD patterns of the Zn₂SiO₄:Mn²⁺ samples heated for different time.

When CTAB as the surfactant molecules was added in the hydrothermal procedure, it was found that the size and the morphology of the $Zn_2SiO_4:Mn^{2+}$ phosphors could be controlled as shown in Fig. 22 a-d. When the CTAB/TEOS=0.01 was adopted, the rod-like particles show the trends to the sphere-like shaped (Fig. 22b). This is an interim morphology from rod-like to spheres. When the concentration of CTAB increased to CTAB/TEOS=0.05, TEM micrograph (Fig. 22c) shows that the willemite phosphors are nano-spheres with the diameter about 60 nm. The nanoparticles dispersed well without agglomerated. When larger amount of CTAB are introduced, nanoparticles aggregates can be observed in the final products. It was known that the surfactant molecules could adsorb on the surface of particles and stabilize the particle by either electrostatic repulsion or steric force. Therefore, the particle size and shape of $Zn_2SiO_4:Mn^{2+}$ nanoparticles would be limited and controlled by the presence of CTAB in the hydrothermal procedure as shown in Fig. 22.



Fig. 22. TEM micrographs of the $Zn_2SiO_4:Mn^{2+}$ samples synthesized at different conditions. (a) Without CTAB, (b) CTAB/TEOS = 0.01, (c) CTAB/TEOS = 0.05, (d) CTAB/TEOS = 0.20.

The relative PL intensities of $Zn_2SiO_4:Mn^{2+}$ samples at different temperatures for different time under the 147 nm excitation are given in Fig. 23. Fig. 23a is for the samples synthesized at different temperatures for 4 hours and Fig. 23b is for the samples heated for different time at 220 °C. The strongest broad band emission at about 523 nm was observed both in Figs. 23a and b, which is attributed to the 4T1-6A1 transition of Mn^{2+} . It shows that the luminescence intensity increase when the temperature and the time increases. We ascribe this phenomenon to the higher crystallinity according to the XRD results as discussed previously.



Fig. 23. Emission spectra of the Zn₂SiO₄:Mn²⁺ samples under 147 excitation: (a) samples prepared at different temperatures for 4 hours and (b) samples heated for different time at 220°C.

The PL intensity among different morphology of the phosphors was also investigated. Fig. 24 presents emission spectra for the samples with different morphology under VUV excitation. The green luminescence is the conventional green of $Zn_2SiO_4:Mn^{2+}$ phosphor, occurring at about 523 nm. As can be seen in Fig. 24, the shape change of phosphors has a certain extent influence on their luminescent intensity. It can be seen that the highest PL intensity was obtained when the $Zn_2SiO_4:Mn^{2+}$ phosphor has uniform spherical morphology (sample c) due to the unique properties of sphere morphology.



Fig. 24. Emission spectra of the $Zn_2SiO_4:Mn^{2+}$ samples: (a) without CTAB, (b) CTAB/TEOS = 0.01, (c) CTAB/TEOS = 0.05, (d) CTAB/TEOS = 0.20.

3.2 Improved PL properties of Zn_2SiO_4 :Mn²⁺ nanophosphors

To improve the luminescence intensity of $Zn_2SiO_4:Mn^{2+}$ nanophosphors, we carried out a heat treatment to the hydrothermally prepared spherical sample. Fig. 25 is the XRD patterns of the samples heat treated at different temperature. The relative diffraction intensity increased when the heat-treatment temperature increased, which indicated that the crystallinity of phosphor is improved by heat treatment.



Fig. 25. XRD patterns of the Zn₂SiO₄:Mn²⁺ samples post treatment at different temperature.

Fig. 26 is the TEM micrograph and size histograms of the Zn_2SiO_4 : Mn^{2+} samples derived from hydrothermal method and post heat treated at 1300°C, Fig. 26a is the TEM micrograph of a typical morphology of Zn_2SiO_4 : Mn^{2+} samples derived from hydrothermal method. It can be

seen that the Zn₂SiO₄:Mn²⁺ nanophosphors have spherical and uniform morphology. After post heat treated at 1300°C, these Zn₂SiO₄:Mn²⁺ nanophosphors keep the spherical shape, fine particle size and monodispersed characteristics as shown in Fig. 26b. Fig. 26c and d are the size histograms of specimens estimating the longest dimension for over 100 particles of samples shown in Fig. 26a and b. The mean diameter is $55\pm25\%$ and $85\pm15\%$ nm of these samples, respectively. As a conclusion, spherical Zn₂SiO₄:Mn²⁺ nanophosphor with monodispersed morphology could be synthesized by this hydrothermal and post treatment process.



Fig. 26. TEM graphs of $Zn_2SiO_4:Mn^{2+}$ nanophosphor samples derived from hydrothermal method (a) and post heat treated at 1300°C (b). Size histograms of $Zn_2SiO_4:Mn^{2+}$ nanophosphor samples derived from hydrothermal method (c) and post heat treated at 1300°C (d).

Fig. 27 shows the relative PL intensity of $Zn_2SiO_4:Mn^{2+}$ nanophosphors after post treatment under the 147nm excitation. As can be seen in Fig. 27, the luminescence intensity about 525nm increases when the heat-treatment temperature increases, which could be ascribed to the improved crystallinity as seen in XRD section. The $Zn_2SiO_4:Mn^{2+}$ nanophosphors post heat treated at 1300°C has the maximum PL intensity, which is 86% of the commercial bulk phosphor (KX-502). Additionally, compared with commercial phosphor, PL peak of our samples located at the shorter wavelength. Because the energy band structure in nanoparticles is different from that of commercial bulk phosphor, the broadened energy gap in nanoscale phosphor⁵⁷ result in the emission peaks of Mn²⁺ blue shift (4 nm) compared with commercial bulk phosphor.

Fig. 28 shows the decay curves of Zn₂SiO₄:Mn²⁺ nanophosphors post treatment at different temperatures. The mean decay time ($\tau_{1/e}$) of the Zn₂SiO₄:Mn²⁺ nanophosphor is elongated from 6.248 to 9.451ms conspicuously when the heat-treatment temperature increased from 1100 °C to 1300 °C. However, the decay time of Zn₂SiO₄:Mn²⁺ particles after post treatment is longer than the commercial product 5.221 ms.



Fig. 27. Emission spectra of Zn₂SiO₄:Mn²⁺ nanophosphor post treated at different temperatures and commercial phosphor



Fig. 28. Decay curves of Zn₂SiO₄:Mn²⁺ nanophosphor post treated at different temperatures.

Some dopants such as Mg^{2+} , Ba^{2+} , Pb^{2+} , Li^+/Al^{3+} or Ga^{3+} are found to affect the decay and efficiency of Mn^{2+} in some degree when substituted for Zn^{2+} or Si^{4+} sites in bulk Zn2SiO4:Mn²⁺ phosphor.⁵⁸⁻⁶² To optimize the PL properties of Zn₂SiO₄:Mn²⁺ nanophosphors, Mg^{2+} , Ca^{2+} , Sr^{2+} and Ba^{2+} are co-doped. Fig. 29 shows XRD patterns of co-doped Zn₂SiO₄:Mn²⁺, A^{2+} (A =Mg, Ca, Sr or Ba) nanophosphors. As shown in Fig. 29, no obvious impurity phase can be detected. Doping A^{2+} in the Zn₂SiO₄ lattice causes the diffraction peaks shift to lower 2 θ positions. The changes of lattice parameter and the unit cell volume of the co-doped Zn₂SiO₄:Mn²⁺, A^{2+} nanophosphors are shown in Tab. 6. It is clear that when A^{2+} are co-doped, both the lattice parameter and unit cell volume increase with the increased ionic radius of the A^{2+} , which attribute to substitution of A^{2+} for Zn²⁺.



Fig. 29. XRD patterns of the Zn₂SiO₄:Mn²⁺ samples co-doped with Mg²⁺, Ca²⁺, Sr²⁺ or Ba²⁺ ions.

Zn ₂ SiO ₄ : Mn ²⁺ , A ²⁺	Lattice para	Unit cell	
	а	с	volume (mir)
Zn ₂ SiO ₄ : Mn ²⁺	1.3928(6)	0.9310(5)	1.56433
Zn ₂ SiO ₄ : Mn ²⁺ ,Mg ²⁺	1.3932(4)	0.9321(9)	1.57031
Zn ₂ SiO ₄ : Mn ²⁺ ,Ca ²⁺	1.3954(0)	0.9322(8)	1.57200
Zn ₂ SiO ₄ : Mn ²⁺ , Sr ²⁺	1.3955(1)	0.9326(0)	1.57286
Zn ₂ SiO ₄ : Mn ²⁺ , Ba ²⁺	1.3955(2)	0.9327(9)	1.57290

Table 6. Lattice parameter and unit cell volume of Zn₂SiO₄:Mn²⁺, A²⁺.

The influence of the co-doped A²⁺ on the PL properties of Zn₂SiO₄:Mn²⁺ nanophosphors is shown in Fig. 30. Under 147nm excitation, the PL intensity of Zn₂SiO₄:Mn²⁺, A²⁺ (A =Mg, Ca, Sr or Ba) nanophosphors exhibit green emission which has been assigned to an electronic transition of ⁴T1 (4G) \rightarrow ⁶A1 (6S) peaking around the wavelength 525nm and which is a spin and parity forbidden emission transition of Mn²⁺. The PL intensity of Zn₂SiO₄:Mn²⁺, A²⁺ (A =Mg, Ca, Sr or Ba) is obviously superior to that of non-codoped samples. Among these samples, the optimum PL intensity of Zn₂SiO₄:Mn²⁺, Ca²⁺ is 107% of that of commercial phosphors. This indicates that the co-doped ions do affect radiative transition probabilities and energy transfer characteristics between excited Mn^{2+} . The co-doped ions of A^{2+} give rise to lattice parameter increased and Zn_2SiO_4 crystal lattice expansion. This distortion of Zn_2SiO_4 lattice results in the double forbidden transition of ${}^{4}T1$ (4G) \rightarrow 6A1 (6S) of Mn^{2+} relieved to some extent, then the emission of Mn^{2+} could be improved as shown in Fig. 30. Fig. 31 shows the decay curves of $Zn_2SiO_4:Mn^{2+}$, A^{2+} (A =Mg, Ca, Sr or Ba) nanophosphor and commercial phosphor under 147nm excitation. The decay time of Mg²⁺ co-doped $Zn_2SiO_4:Mn^{2+}$ is 4.981 ms, which is much shorter than the commercial bulk phosphor. This decay time could be favorable for PDP application. However, Ca^{2+} , Sr^{2+} , Ba^{2+} co-doped samples have much longer decay time, 6.378 ms, 6.472ms and 7.529 ms, respectively. The inset of Fig. 31 exhibits the relative intensity and decay time of $Zn_2SiO_4:Mn^{2+}$ improved by the co-doping of A^{2+} .



Fig. 30. Emission spectra of $Zn_2SiO_4:Mn^{2+}$, A^{2+} (A = Mg, Ca, Sr, Ba) nanophosphor under 147nm excitation.

3.3 Unique PL properties of Zn₂SiO₄: Mn²⁺ nanophosphors

We could control the particle sizes of the uniform $Zn_2SiO_4:Mn^{2+}$ nanophosphors via the hydrothermal method by adjusting the surfactant amount and the hydrothermal temperature as shown in Fig. 32. Interesting finding is that with the decrease of particle size, the concentration quenching occurs at different Mn^{2+} concentration exhibited in Fig. 33.



Fig. 31. Decay curves of $Zn_2SiO_4:Mn^{2+}$, A^{2+} (A =Mg, Ca, Sr, Ba) nanophosphor at 147nm excitation. Inset, efficiency and decay time of $Zn_2SiO_4:Mn^{2+}$, A^{2+} (A=Mg, Ca, Sr, Ba) nanophosphor and commercial phosphor.



Fig. 32. TEM micrographs of the Zn₂SiO₄:Mn²⁺ samples synthesized at different hydrothermal conditions. (a) ×CTAB, (b) ×2CTAB, (c) ×3CTAB at hydrothermal temperature 220°C. (d) ×3CTAB at hydrothermal temperature 180°C, (e) ×3CTAB at hydrothermal temperature 140°C.



Fig. 33. Emission spectra of $Zn_{2-x}SiO_4$: xMn nanophosphors with different particle sizes under 147 nm excitation.



Fig. 34. Normalized decay curves of $Zn_{2-x}SiO_4$: xMn (x=0.12) nanophosphors with different particle sizes.

In Zn_{2-x}Mn_xSiO₄ of 60 nm, when x= 0.06, the sample shows strongest PL emission, while when the particle size decreased to 10 nm, it occurs at x=0.18. As we know, when the rate of nonradiative transitions surpassed that of radiative ones, the concentration quenching occurs. Because there existed quantities of grain boundaries in nanosized particles, which made the energy of excitation confined in almost "isolated" unit of Mn²⁺, that is, the rate of nonradiative transitions was suppressed for the resonant energy transfer between Mn²⁺ ions. Therefore, the concentration of quenching in the Zn₂SiO₄:Mn²⁺ nanophosphors increased when the particles decreased. Decay time of $Zn_2SiO_4:Mn^{2+}$ nanophosphor prolonged with decrease particle sizes due to the exchange interaction between Mn^{2+} ions decreased as shown in Fig. 34. These results indicate that particle sizes of nanophosphors played an important role in the changes of photoluminescence properties of $Zn_2SiO_4:Mn^{2+}$ under vuv excitation.

4. Blue phosphor of BaMgAl₁₀O₁₇:Eu²⁺

BaMgAl₁₀O₁₇:Eu²⁺ (BAM), as an efficient blue-emission phosphor, has been widely used in PDPs, FEDs, and fluorescence lamps (FLs).^{63,64} BAM phosphors are usually prepared by the solid-state reaction. In this process, high-temperature heating is necessary, and the phosphors have a large size range and irregular shapes. It is reported that an increase in temperature leads to an increased particle size and surface morphology.⁶⁵ As nano-phosphors have small size effect, surface effect, and the quantum size effect, they present different optical and electrical properties.⁶⁶ Besides, for the application, nano-phosphors are easy to brush screen and get higher resolution to make the pictures more vivid. Thus, it is necessary to obtain nanosized BAM phosphors with low reaction temperature. As sol-gel method is an efficient technique for preparation of nanosized materials, we adopt it to synthesize BAM nanophosphor and investigate the photoluminescence in VUV region.

4.1 Controllable morphology of BAM nanophosphors

Fig. 35 shows the typical XRD patterns of the BaMgAl₁₀O₁₇:Eu²⁺ samples by sol-gel method under different temperatures for 4 h. At 850°C, the sample was amorphous. When the temperature rose to 1,200°C, the BAM phase began to form but still had an impurity peak (BaAl₂O₄). When the temperature increased to 1,250°C, the impurity peak disappeared and formed a good BAM phase. It matched well with the JCPDF (26-0163) files of BAM. After further improve the reaction temperature to 1300°C, the crystalline was also single-phase and the crystallinity was much enhanced. On the contrary to this technique, in conventional solid-state reaction, the presence of intermediates was identified which brought on impurities in the product even at the temperature of 1600°C.⁶⁷



Fig. 35. XRD patterns for BaMgAl₁₀O₁₇:Eu²⁺ at different temperatures.

Fig. 36 exhibits the SEM micrographs of the BAM samples under 1250°C (a) and 1300°C (b). As BaMgAl₁₀O₁₇ has the crystal structure of β -alumina, the particle takes the form of hexagonal platelets when the crystal freely grows,⁶⁸ but from the images, the nanorods can be obviously seen and have a homogeneous grain size at 80–100 nm in diameter and 0.8–1 µm in length. This morphology is different from that of samples synthesized by other methods that result in irregular morphology, such as the solid-state method,⁶⁹ oxalate coprecipitation process,^{70,71} and microwave irradiation synthesis methods.⁷² The advantages of sol-gel method could be responsible for this phenomenon, such as good mixing of starting materials in molecular level, limiting reaction space and relatively low reaction temperature.⁷³



Fig. 36. SEM images of BAM phosphors synthesized at (a) 1250°C and (b) 1300°C.

It has been reported in the systems of ZnO and ZnSiO₄: Mn that the addition of cetyl-trimethyl-ammonium bromide (CTAB) in sol-gel process could improve their luminescent intensity attributing to the interaction between CTA⁺ and anionic group.^{14,74,75} Fig. 37 shows the typical XRD patterns of the BaMgAl₁₀O₁₇:Eu²⁺ phosphors synthesized at 1300°C with different concentration of CTAB. All of the peaks can be indexed and they match well with JCPDF (26-0163) file of BAM. The result indicates the phosphor obtained by sol-gel process is monophasic BAM ascribing to the well disperse of the precursor powder.

To investigate the effect of CTAB on the morphology of BAM crystalline, the SEM images of the samples with adding CTAB is investigated in Fig. 38. From the micrographs, the sample

derived from CTAB assisted sol-gel process exhibits the morphology of nanosheets with about 100nm in thickness. It shows that the morphology of BAM derived from sol-gel method can be altered by the addition of surfactant CTAB. As $BaMgAl_{10}O_{17}$ has the crystal structure of β -alumina, the particle conventionally takes the form of hexagonal platelets when the crystal freely grows. The different morphologies in this work and the phenomenon of the alteration from rods to sheets (as shown in Fig. 36 and Fig. 38) could be explained by the BAM crystal growth mechanisms of different procedures.



Fig. 37. Typical XRD patterns of the $BaMgAl_{10}O_{17}$: Eu^{2+} phosphors synthesized at 1300°C with different concentration of CTAB.



Fig. 38. SEM image of the sample synthesized with adding CTAB.

The crystal growth mechanisms of BAM derived from sol-gel process can be illustrated in Fig. 39. Fig. 39a depicts the formation process of BAM nano-rods, and Fig. 39b presents the mechanisms of the formation of nano-sheets while CTAB is added. In the route (a), first, all metal ions in the initial solution are in hydration state, which reject with the hydrogen ions in the water leading to a series of hydrolysis reactions (as shown in equation 1). After the

metal ions hydrolyzing in the form of precipitation, it could be dissolved with the adding of citric acid, which is called precipitation-peptization reaction (as shown in equation 2). In these reactions, the colloid seeds are produced, which is positive charge covering with anions of equal charge.





$$M(H_2O)_{x^{2+}} = M(H_2O)_{x-1}(OH)^{(z-1)} + H^+ - M(OH)_n$$
(1)

$$a [M(OH)_n (H_2O)_x]^0 + b C_6 H_8 O_7 = \{ [M(OH)_n (H_2O)_x]_a H_b \}^{b+} + b C_6 H_7 O_7^{-}$$
(2)

The colloid seeds in this process are $\{[M(OH)_n(H_2O)_x]_aH_b\}^{b+}$ covered by $C_6H_7O_7$ due to the Coulomb's force. Therefore, the reaction of the formation of BAM phase is limited in the space. By calcination, the anions on the surface could be decomposed into CO₂ and H₂O and BAM nano-rods could be produced via calcination (as shown in Fig. 36 (a)). It has been known that the adsorption of units on crystal surfaces strongly affects the growth speed and orientation of crystals.^{69,76} When cationic surfactant CTAB is introduced in this process, the positive charge CTA⁺ ion could carry the anions on the surface of the colloid seeds by electrostatic interaction, which makes the BAM crystalline grow in the direction of absent anions when calcined (as shown in Fig. 38 (b)). This difference could be responsible for the alternation of the morphology from rods to sheets. by calcination and forms the morphology of sheets (as shown in Fig. 38).

4.2 Improvement PL performance of BAM nanophosphors

Fig. 40 illustrates the comparison of the emission spectra among commercial $BaMgAl_{10}O_{17}$:Eu²⁺ blue phosphor and nano-phosphors synthesized by the sol-gel method under 1,300 and 1,250°C by 147 nm excitation. As shown in Fig. 40, a broad emission band can be seen, and the peak is located at 452 nm. It is attributed to the 4f⁶5d \rightarrow 4f⁷ (⁸S_{7/2}) transition of Eu²⁺. With the temperature increasing from 1,250 to 1,300°C, the emission intensity of these nano-phosphors by 147 nm excited enhanced about 22%, and the intensity of the nano-phosphor synthesized by the sol-gel method at 1,300°C was 78.15% of the commercial phosphor.

From Fig. 40, the nano-phosphors have perfect photoluminescence properties. As Maas *et al.*³³ reported that phosphors prepared by the wet chemical method had poor photoluminescence, this high intensity may be due to the increased specific surface area when nano-size phosphors are prepared and the relatively high synthesized temperature – compared with the hydrothermal method – at which the residual organic ions can be removed.

The photoluminescence intensity of the samples was strongly affected by the doping concentration of Eu²⁺. To investigate the optimum Eu²⁺ concentration in this process, the relative emission intensity dependence of Ba_{1-x}MgAl₁₀O₁₇:xEu²⁺ excited by 147 nm was evaluated. Fig. 41 exhibits the emission spectra of Ba_{1-x}MgAl₁₀O₁₇:xEu²⁺ (0.06 $\leq x \leq$ 0.14) synthesized by the sol-gel method at 1,300°C ($\lambda_{ex} = 147$ nm). The result indicates that the most intense band is observed at a content of x = 0.1 and the intensity decreases in Ba_{1-x}MgAl₁₀O₁₇:xEu²⁺ (x = 0.06, 0.08, 0.12, 0.14), which is called the concentration quenching phenomenon.⁷⁷ The same phenomenon occurred when excited by 254 nm. Therefore, the optimum chemical composition is Ba_{0.9} MgAl₁₀O₁₇:0.1Eu²⁺ in the sol-gel process.



Fig. 40. Emission spectra of commercial BaMgAl₁₀O₁₇:Eu²⁺ blue phosphor and nanophosphors synthesized by sol-gel method under 1,300°C and 1,250°C (λ_{ex} = 147 nm)



Fig. 41. Emission spectra of Ba_{1-x}MgAl₁₀O₁₇:xEu²⁺ ($0.06 \le x \le 0.14$) synthesized by sol-gel method at 1300°C ($\lambda_{ex} = 147 \text{ nm}$)

The color coordinates of commercial BaMgAl₁₀O₁₇:Eu²⁺ blue phosphor and nano-phosphors synthesized by the sol-gel method under 1,300°C and 1,250°C by 147 nm and 254 nm excitation are exhibited in Tab. 7. It can be found that the y value in color coordinates of the samples prepared by the sol-gel process is much lower than that of standard blue fluorescence. These low y values indicate that the nanophosphor is useful for restricting the decrease of BAM effciency during heating and the fitting y value should between 0.06 and 0.1.^{78,79}

Samples	Coordinates (λ _{ex} =147nm)	Coordinates (λ _{ex} =254nm)
Commercial phosphor	(0.144, 0.069)	(0.144, 0.068)
Sol-gel 1250°C	(0.145, 0.063)	(0.144, 0.065)
Sol-gel 1,300°C	(0.143, 0.068)	(0.145, 0.062)
NTSC, blue	(0.14, 0.08)	. ,

Table 7. The color coordinates of samples under UV and VUV excitation

However, the luminescence intensity and thermal stability of the BAM nanorods in VUV region still could not meet the requirement of the commercial use. Futher improvements on the nanorods are necessary. In the systems of ZnO and ZnSiO₄: Mn, it was found that the addition of cetyl-tri-methyl-ammonium bromide (CTAB) in sol-gel process could improve their luminescent intensity attributing to the interaction between CTA⁺ and anionic group.^{14,74,75} Moreover, the doping of Mg²⁺ to substitute Al³⁺ in the bulk BAM could effectively restrain the thermal degradation.⁸⁰ Hence Mg²⁺ and CTAB were introduced in sol-gel method for synthesizing BAM nanophosphor.



Fig. 42. Emission spectrum of BAM nanorods doped with 2% CTAB by 147 nm excitation (solid line); The dashed line exhibits the Gaussian fitting result of the spectrum; The inset is the relative emission intensity of the nanophosphors with different concentration of CTAB.

Fig. 42 shows the emission spectrum of BAM nanorods doped with 2% CTAB (λ_{ex} = 147 nm). The emission spectrum presents a broad band locating at about 452 nm, which attributes to the 4f⁶5d \rightarrow 4f⁷(⁸S_{7/2}) transition of Eu²⁺. The band is of asymmetrical distribution which relates to the different sites that Eu²⁺ occupy in BAM. By Gaussian fitting the VUV emission spectrum, three peaks are found locating at 446nm, 477nm and 517nm, respectively, corresponding to the emission of Eu²⁺ in the sites of BR, a-BR and spinel layer.⁸¹⁻⁸³ To probe into the influence of CTAB on VUV emission intensity, the luminescent properties of the nanorods with different concentration of CTAB are depicted under 147 nm excitation. From the inset of Fig. 43, it can be seen that the addition of CTAB evidently enhances the relative intensity of the nanophosphor. The optimum concentration of CTAB is determined to be 2 %, which heightens the original emission intensity about 16%. This phenomenon could be interpreted by the inherent function of the surfactant CTAB: It could not only reduce the surface tension of solution and lower the energy to form a new phase, but also eliminate the defect states through chemical interaction between surfactants and inorganic species during the synthesis.



Fig. 43. Relative emission intensity of Ba_{0.9}Mg(Al_{1-x}Mg_x)₁₀O_{17-5x}: $0.1Eu^{2+}$ ($0 \le x \le 0.06$) nanophosphors synthesized by 2% CTAB assisted sol-gel technique before and after annealing ($\lambda_{ex} = 147$ nm).

As we know, the blue phosphor BAM could be jeopardized by the thermal degradation when heated at about 550 °C. The relative emission intensity of the above CTAB-prepared nanorods is valued after a heat-treatment of 550 °C for 1 h in air condition. Their deterioration ratios are 25.3% (0% CTAB), 24.4% (2% CTAB), 24.9% (4% CTAB) and 25.5% (6% CTAB), respectively. So the addition of CTAB in the sol-gel process does not affect the thermal stability of the BAM nanorods.

For the purpose of getting BAM nanophosphor with high emission intensity and good thermal stability, Mg²⁺ was introduced in the host on the basis of adding 2% CTAB. Fig. 43

presents the relative emission intensity of BAM nanophosphors with the variation of doping Mg²⁺ before and after annealing (λ_{ex} = 147 nm). It can be obviously found that the additional of Mg2+ in the sites of Al3+ could further enhance the emission intensity of BAM nanophosphor before and after annealing. The optimum concentration of Mg^{2+} is 4%. On one hand, due to Mg-O has absorption in VUV region, the doping of additional Mg²⁺ could enhance the emission intensity of BAM phosphor. On the other hand, since the substitution of Mg^{2+} for Al^{3+} is a substitution of lower valence cations for higher valence cations, considering the charge compensating mechanism, anion vacancies or interstitial cations must be generated in the beta alumina structure; These defects play roles on the quenching centers and decrease the emission intensity. As a result, the optimum doping concentration of Mg^{2+} is affected by the above two reasons. The thermal degradation of the optimum nanophosphor (with the addition of 2% CTAB and 4% Mg) is calculated to be 18.5%, which may be compared to a value of 6% with a nanophosphor synthesized with only 2% CTAB. To analyze the improvement of the thermal stability, the changes of full-width at halfmaximum (FWHM) and y value of color coordinates of the samples synthesized with 2% CTAB and different concentrations of Mg2+ are shown in Fig. 44. As mentioned in Fig. 45a, the emission spectrum of BAM is composed of three emission bands which correspond to Eu^{2+} in different sites of Ba^{2+} . With the variation of the distribution of Eu^{2+} in the three sites, the color coordinates and FWHM could change synchronously. As a result, the variations in Fig. 44 reflect the lattice environment of Eu^{2+} is changed by doping Mg²⁺. The y value of the emissions for Eu^{2+} in three sites is different that it decreases with decreasing wavelength. Therefore, the decrease of y value with increasing the doping concentration of Mg^{2+} (as shown in Fig. 44) indicates that Eu^{2+} migrate from the sites emitting long wavelength (spinel block) to those emitting short wavelength (mirror layer). Associated with the consideration that the migration of Eu²⁺ in BAM from mirror planes to spinel blocks is another essential mechanism of the thermal degradation besides the oxidation of Eu²⁺ to Eu³⁺,⁸⁴ the introduction of Mg2+ to substitute Al3+ will certainly improve its thermal stability.



Fig. 44. FWHM and y value of color coordinates of the samples synthesized with 2% CTAB and different concentration of Mg²⁺.



Fig. 45. Emission spectra of BAM samples: (a) commercial phosphor, before annealing, (b) optimum nanorods, before annealing, (c) commercial phosphor, after annealing, (d) optimum nanorods, after annealing (λ_{ex} =147nm); The inset is the columnar graph of the emission intensity.

Therefore, the optimum nanoscaled BAM is that synthesized by 2% CTAB assisted sol-gel method with 4% Mg²⁺ doped. The comparison between the optimum nanorods and commercial BAM phosphor (kx-501) on emission intensity and thermal stability are illustrated in Fig.45 (λ_{ex} = 147 nm). Before annealing, the luminescence intensity of the nanorods is nearly 92% of that of the commercial phosphor. After annealing, the luminescence intensity of the nanorods is nearly 97% of that of the annealed commercial phosphor. These data reflect that the thermal stability of the nanorods is superior to that of the commercial phosphor, and the BAM nanorods could be potentially applied in high resolution plasma display panels.

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Mechanochemically Synthesized Metallic-Ceramic Nanocomposite; Mechanisms and Properties

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1. Introduction

Solid state chemical reaction is attributed to the chemical reaction performed at temperature which reactants are solid. In most solid state chemical reactions the reaction volume continually diminishes as the reactants become spatially separated by the products. As a result, the kinetics of solid state chemical reactions are limited by the rate at which reactant species are able to diffuse across phase boundaries and through intervening product layers. Hence, the conventional solid state technique invariably require the use of high processing temperatures to ensure that diffusion rate is maintained at a high level (Schmalzried, 1995), (Stein et al., 1993). On the other hand, high temperature process invariably leads to formation of coarse-grained products due to the occurrence of grain growth. Such coarse-grained materials are generally undesirable for manufacturing advanced engineering components due to their problems such as poor mechanical properties, poor sinterability, and etc. Consequently, there is considerable interest in alternative synthesis techniques that either reduce the required processing temperature or eliminate the need for applied heating altogether (McCormick, 1995), (McCormick & Froes, 1998).

Mechanical milling has been recognized as an effective way of occurrence the solid state chemical reaction at low temperature. This process is considered as a means to mechanically induced solid state chemical reaction that occur in precursors powder mixture during collision in the grinding media (Suryanarayana, 2001). Mechanical milling could be classified as mechanical grinding, mechanical alloying (MA), and Mechanochemical synthesis (MCS) according to the precursors powder mixture as well as structural and chemical changes that occur during milling. The milling process that there is no change in chemical composition of precursors is attributed to the mechanical grinding. The mechanical alloying is refers to the formation of alloys by milling of precursors changes as a result of mechanically induced solid state reaction. This process is also termed as reactive milling (Suryanarayana, 2001), (Takas, 2002).

In this chapter book, the fundamental and mechanisms of mechanochemical process is presented and the recent developments in mechanochemically synthesized metallic-ceramic nanocomposite are overeviewed.

2. Milling equipments

Mechanical milling usually performed using ball milling equipments that generally divided to "low energy" and "high energy" category based on the value of induced the mechanical energy to the powder mixture. The ball milling equipments used for mechanical grinding or mixing are low energy such as Horizontal mill. In mechanical milling processes that utilize to change the chemical composition of precursors, the high energy ball milling equipments is generally used. Mechanochemical reaction can be performed in various types of high energy ball mills, including attrition, planetary, and vibratory mills that schematically shown in Fig. 1.



Fig. 1. Various types of high energy ball mills: (a) planetary mill, (b) attrition mill, (c) 1D vibratory mill, and (d) 3D vibratory mill (Suryanarayana, 2001).

In an attrition mill, the rotating impeller cause to relative movement between balls and powders. In a planetary ball mill, a rotating disc and vials revolve in opposite direction in order of several hundred rpm. A trade name of Fritsch is an example of the planetary mills. In a 1D vibratory mill that also known as a shaker mill, the vessel is set in vertical oscillatory motion. 3D vibratory mills consist of vials which shake at s frequency about 20 Hz in a "figure-eight" trajectory. Spex 8000 is a commercial type of 3D vibratory mills. The mechanical energy that induced by attrition mills is significantly lower that planetary or vibratory mills. However, unlike planetary and vibratory mills, attrition mills are readily amenable to scale up, which allows mass production of powders through mechanochemical process (Suryanarayana, 2001).

3. Reaction kinetics of mechanochemical synthesis

The mechanochemical reactions are characterized by a large negative free energy change at room temperature and are therefore thermodynamically feasible at room temperature. However, commercial operations by the pyrometallurgical techniques are conducted at elevated temperature to overcome the kinetic barriers and achieve sufficiently high reaction rates whereas; mechanochemical process can be used more generally to promote chemical reactions. The underlying mechanism of mechanochemical process is repeated deformation, fracture, and welding of the powder charge during collisions of the grinding media. Fracture of particles exposes fresh reacting surfaces and welding generates interfaces between reactant phases across which short-range diffusion can occur, thus allowing chemical reactions to take place without kinetic constraint. Diffusion rates are also enhanced by the high concentration of lattice defects, which provide "short circuit" diffusion paths (Schaffer & McCormick, 1990), (Forrester & Schaffer, 1995).

Mechanochemical reaction could be done by two different reactions kinetics, "gradual" or "sudden" reaction, depending on nature of precursors (magnitude of enthalpy change during chemical reaction) as well as milling condition. If the enthalpy change associated with the formation of the product phases is low, then the heat generated will be insufficient to significantly influence the reaction kinetics. Therefore, reaction will proceed in a gradual manner. Gradual mechanochemical reaction systems have generally been found to exhibit sigmoidal reaction kinetics. The reaction rate initially increases with milling due to increasing activation and microstructural refinement of the reactants. The reaction rate then reaches a maximum at an intermediate milling time before decreasing as the reaction approaches completion due to dilution of the reactants by the product phases (Forrester & Schaffer, 1995). The sudden reactions take place as a self-propagating combustion reaction when the reaction enthalpy is sufficiently high. Combustion during milling is detected experimentally by the temperature spike associated with a sudden release of heat (Takacs, 2002). Fig. 2 shows the variation in temperature of a milling vial during processing of a highly exothermic reactant mixture. In the initial stages of milling, the temperature gradually increases up to a steadystate value as a result of heat generated by collisions of the grinding media. Following the critical milling time, depending on the milling condition for same precursors, the vial temperature suddenly increases due to the heat generated by combustion of the reactants. The temperature then slowly decays to the previous steady-state value.



Fig. 2. Vial temperature as a function of time during milling of a combustive reaction system (Takacs, 2002).

Direct observation of ignition and propagation in mechanochemical combustion reaction during milling is also conducted by Deidda et al. (Deidda et al., 2004) using transparent

quartz vials. Fig. 3 shows the quartz vial at different time after starting the milling of the Ta:C=50:50 system. It is observed that the ignition begins after the initial time and then propagates. The local temperature of ignited powder is also recorded by pyrometer and presented as a function of milling time in Fig. 3.



Fig. 3. High speed image sequence of the reaction of Ta:C=50:50 in a quartz vial coupled with the related temperature recording obtained by the infrared thermometer (Deidda et al., 2004).

The modality of displacement reactions can be specified by theoretical adiabatic temperature, T_{ad} , of the reaction. Tad represents the temperature of heat releasing during chemical reaction. A value of T_{ad} >1800K is generally considered to be the minimum necessary temperature for the occurrence of self-propagating combustion in a thermally ignited system (Munir, 1988). In contrast, Schaffer and McCormick (Schaffer & McCormick, 1990) showed that a value of T_{ad} >1300K is adequate for the sudden occurrence of chemical reaction during ball milling. The Tad value could be estimated from the following relation:

$$\Delta H_{r} + \sum_{T_{i}} \int_{T_{i}}^{T_{m}} C_{p} + \sum_{i} \Delta H_{t} + \sum_{i} \int_{T_{m}}^{T_{ad}} C_{p} = 0$$
(1)

Where ΔH_r is the heat of reaction, T_i is the initial temperature, the T_m 's are the melting points of products, the sC_p 's are the molar heat capacities of the solid products, ΔH_t 's are the heat of transitions of the products and lC_p 's are the molar heat capacities of the liquid products. It should be noted that the last term in relation 1 is ignored if $T_{ad} < T_m$'s.

The experimental combustion temperature for several systems (recorded by pyrometer technique (Deidda, 2004)) and theoretical T_{ad} are presented in Table 1. As seen, the pyrometer recorded temperature of combustion reaction during milling is invariably close to the calculated T_{ad} .

Chemical system	Adiabatic temperature, T _{ad} (K)	Combustion temperature, T_c (K)
Ti ₅ Si ₃	2550	2420
TiSi	2370	1818
Ti5Si4	2193	2063
TiSi ₂	1829	1613
Ti ₇₀ C ₃₀	1991	2183
Ti ₆₀ C ₄₀	2614	2773
Ti50C50	3206	>2873
Ta ₅₀ C ₅₀	2901	2870

Table 1. The experimental combustion temperature and the calculated adiabatic temperature for the various systems (Deidda et al., 2004).

4. Mechanochemical synthesis

It was recognized in 1989 that ball milling could be used to induce a solid state chemical reaction by demonstrating that the pure metal Cu can be synthesized when CuO and Ca were ball milled together at room temperature. Simultaneous reduction of CuO and ZnO by Ca has also been shown to result in the formation of brass (Schaffer & McCormick, 1989), (McCormick et al., 1989). After that the extensive researches for preparing other metals such as Fe, Ti, Zr, W, and etc. were performed. The mechanochemical reactions could be divided to two categories involve non-displacement and displacement chemical reactions. Non-displacement reactions are the chemical reaction occurred in the reactants in order to combine the elements to produce final phases. This process is similar to mechanical alloying. In displacement reaction, the reactants react to each others with exchange the element between them to form new phases. Most of the mechanochemical reactions studied have been displacement reactions of the type:

$$MO + R \rightarrow M + RO$$
 (2)

Where a metal oxide (MO) is reduced by a more reactive metal (reductant, R) to the pure metal M. Metal chlorides and sulfides have also been reduced to pure metals this way. The products of displacement reactions normally consist of two phases, the metal (or a compound) and the oxide, chloride, or sulfide associated with the reactant. For preparing pure metallic phase, the by-product must be removed by removal processes such as

leaching. The removal of one of the phases produced by mechanochemical reaction may be difficult due to the high reactivity of the metallic phase associated with nanocrystalline structure and intermixing of the phases induced by mechanical forces (El-Eskandarany, 2001a). Therefore, utilizing the products of mechanochemical reaction to fabricate the composite structures could be useful to change the properties of each phase. Since, unlike chlorides and sulfides, the oxide phases could be used in structural application, the most mechanochemical reactions to synthesize composite structure have been used the reduction of oxide phase. Mechanochemically synthesized component with more than two phases offers a number of advantages over the conventional metal processing techniques. First it is enable to reduce a number of oxides and halides to desired compound at room temperature, thus it is cost effective. Second, if a number of components are reduced simultaneously, then it is possible to produce an alloy without first having to convert the oxides to pure metals and then to desired alloy. Third, for powder metallurgy application, it allows the direct formation of powder product. Fourth, severe plastic deformation induced during high energy ball milling cause to formation of nanocrystalline structure. Finally, the mechanochemically synthesized phases especially trough displacement reaction are chemically compatible (Suryanarayana, 2001), (Takacs, 2002).

Recently, synthesis of metallic-ceramic composite powder through mechanochemical reaction is considered because of advantages mentioned above. In this area, the ceramic (metallic) phase especially considered as reinforcement (tougher) for metallic (ceramic) phase to enhance its properties. This chapter presents an overview of the recent developments in mechanochemically synthesized metallic-ceramic nanocomposite consist of metal-ceramic and Intermetallic-ceramic trough displacement reaction.

4.1 Metal-ceramic nanocomposite

It is well known that the addition of hard ceramic particles to soft metals provides a combination of properties of both metallic matrix and ceramic reinforcement components. This may result in improvement of physical and mechanical properties of the composite (Rajkovic et al., 2008).

Many methods were studied to prepare metal-based composites. The one of methods for preparation of metal-base composite is casting. In this method, particles are added to molten metal by stirring before casting. However, the difference in thermal expansion coefficients between ceramic particles and molten metal constituents and the poor wettability between these two become an obstacle to the liquid method used for synthesizing metal matrix composite (Konopka & Szafran, 2006). Another way of producing both metal-based and ceramic-based composite is using powder metallurgy methods. In powder metallurgy methods, the composite powder is consolidated to producing composite part. In these methods, the powder could be prepared by mixing or reaction of constituents. The preparation of composite powder by mechanochemical reaction is expected an advanced method for fabrication of nanocrystalline part (El-eskandarany, 2001a)

One of the first reports on mechanochemical synthesis of metal-ceramic nanocomposite has been published by Matteazzi and Caer about alumina-iron nanocomposite powders produced by mechanochemical reaction between hematite and aluminum (Matteazzi & Caer, 1992). The mechanochemical reduction of copper oxide with different reductants such as Fe, Al, Ti, Ca, Ni and C has been investigated (Schaffer & McCormick, 1990), (Schaffer & McCormick, 1991). Their products were often a mixture of copper with dispersed oxides particle, i.e. copper matrix composites such as Cu–Al₂O₃ (Wu & Li, 2000), (Ying & Zhang, 2000), (Hwang et al., 2004) (Hwang & Lee, 2005), Cu–ZnO (Hessel et al., 2001), and Cu–MnO (sheibani et al., 2009). One of the most important ceramic particles used in structural application is Al_2O_3 (Ying & Zhang, 2000), (Hwang & Lee, 2005). The presence of fine Al_2O_3 articles in copper matrix leads not only to improve the hardness of this material, but also to decrease the grain growth rate at temperatures even close to the melting point of copper matrix. In this way, the amount, size and distribution of reinforcing particles play a critical role in enhancing or limiting the overall properties of the composite (Rajkovic et al., 2008). Hwang et al. (Hwang et al., 2004) (Hwang & Lee, 2005) synthesized Cu- Al_2O_3 nanocomposite powder by mechanochemical reaction between Cu₂O and Al according to the following reaction:

$$3Cu_2O + 2Al + XCu \rightarrow (6+X)Cu + Al_2O_3$$

The presence of Cu in the precursor powder mixture lead to formation of different amount of Al₂O₃ in the range of 4 to 21 volume percent. XRD pattern of powder mixture as-received and after different milling time are show in Fig. 4.



Fig. 4. XRD pattern of $Cu_2O+Al+Cu$ powder mixture as-received and after different ball milling time (Hwang et al., 2004).

As can be seen, the Cu_2O peaks reduced and only the peaks related to the Cu is remained after milling. There is also no evidence of Al_2O_3 phase on XRD pattern that attributed to the peak broadening as a result of nanocrystalline or highly strained powder.

Transmission Electron microscopy (TEM) of prepared powder after 140 h ball milling was performed for further investigation. Fig. 5 shows TEM bright field (Fig. 5a), dark field (Fig. 5b) and Selected Area Diffraction (SAD) pattern (Fig. 5c) obtained from a small particle of the nanostructural powder after milling for 140 h.

Typical SAD patterns displayed spotty rings which could be indexed as a mixture of FCC Cu and Rhomboheral α -Al₂O₃. The fine structure of the spotty rings indicated that both Cu and α -Al₂O₃ phases took the form of predominantly nanostructural particles. Dark field imaging confirmed this and indicated a bimodal size distribution of nanocrystallites, with an average size of around 2–5 nm for the smaller crystals and around 10–20 nm for the larger ones. A TEM-energy dispersive spectroscopy (EDS) micrograph of the hot pressed samples contained 21 vol.% Al₂O₃ is given in Fig. 6 along with EDS spectra of the dark and bright phases. EDS spectra collected from the phases show that the dark phase is Cu while

the bright phase is Al₂O₃. The crystallite size of both phases in hot pressed 21 vol.% Al₂O₃ sample at different pressing temperatures (800 to 900 °C) reported in the range of 20 to 30 nm. The results of Rockwell hardness tests of hot pressed samples with different vol.% Al₂O₃ (from 4.1 to 20.9) are given in Table 2. The hardness of the hot pressed samples increases from 70 to 103 HRB with increasing vol.% of Al₂O₃. The hardness of the samples is in reasonable proportion to the vol.% of Al₂O₃ formed in Cu matrix.



Fig. 5. TEM images of nanostructural Cu-21 vol.% Al₂O₃ powder particle after 140 h milling time, (a) bright field image, (b) dark field image and (c) SAD pattern (Hwang et al., 2004).

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Fig. 6. TEM bright field image and energy dispersive spectroscopy (EDS) micrograph of the hot pressed Cu- 21 vol.% Al_2O_3 sample (Hwang & Lee, 2005).

Alloy	Hardness number (HR _B)	
HP-4.1	70 ± 4	
HP-11.9	88 ± 2	
HP-15.5	98 ± 3	
HP-20.9	103 ± 1	

Table 2. Rockwell hardness test on the hot pressed samples at 850 $^{\circ}$ C with different vol.% Al₂O₃ from 4.1 to 20.9 (Hwang & Lee, 2005).

It is also reported that a common way of increasing the low intrinsic strength of Cu is alloying with BCC elements such as Mo (Botcharova et al., 2004). Sabooni et al. synthesized the Cu-15Wt.%Mo/30Vol.%Al₂O₃ (Cu(Mo)-Al₂O₃) nanocomposite by mechanochemical reaction between MoO₃ and Al in presence of Cu (Sabooni et al., 2010). The modality of mechanochemical reaction in MoO₃+Al and MoO₃+Al+Cu powder mixture are determined as combustion mode according to the calculated T_{ad} as well as measured vial temperature. Fig. 7 shows the vial temperature during milling for MoO₃+Al (without diluent) and MoO₃+Al+Cu (with Cu as diluent) powder mixture. The presence of Cu leads to decrease the T_{ad} of MoO₃+Al reaction from 4773 to 2361 K and increase the combustion time.

The crystallite size of Cu in Cu(Mo)-Al₂O₃ calculated from XRD pattern using Williamson-Hall method after 60 h ball milling and subsequent annealing were reported about 30 and 50-80 nm, respectively. TEM images of 60 h milled powder presented in Fig. 8 reveal a homogenous dispersion of reinforcements with the size of about 10nm in the matrix. TEM images also approve the nanocrystalline structure of the matrix which had been obtained by Williamson-Hall method. The average microhardness values of pure Cu (Sabooni et al., 2010) and nanostructured Cu (Chen et al., 2006) increases from 39HV to 178 HV as a result of decreasing in crystallite size.





Addition of alloying element of Mo in order to have nanocrystalline solid solution leads to increase hardness to about 198 HV in Cu(Mo) (Sabooni et al., 2010). Finally, incorporation of ceramic nanoparticles in a nanocrystalline matrix of Cu(Mo) leads to high increase of hardness to 307HV in Cu(Mo)-Al₂O₃ (Sabooni et al., 2010) which is about eight times higher than the hardness of pure Cu. Three important strengthening mechanisms are suggested for high value of hardness in Cu(Mo)-Al₂O₃ nanocomposite: reduction of crystallite size, formation of Cu(Mo) solid solution and dispersion hardening of nanometric reinforcements in the nanocrystalline matrix.

Aluminum-based composites are ideal materials for structural applications in the aerospace and automotive industries due to their high strength-to-weight ratio (Clyne & Withers, 1995). Reinforcing the ductile aluminum matrix with stronger and stiffer second-phase reinforcements such as oxides, carbides, borides, and nitrides provides a combination of properties of both the metallic matrix and the ceramic reinforcement components (Piggott, 1980). In recent years, many researchers have paid attention to new fabrication techniques for making aluminum matrix composite. Synthesis of Al based nanocomposites by mechanochemical reaction has recently been examined by some researchers. Shengqi et al. have investigated the mechanochemical reaction of CuO and Al powder (Shengqi et al., 1998). Wu and Li have synthesized nanostructured aluminum matrix composite reinforced with CuAl₂ (100–500 nm in size), Al₂O₃ and Al₄C₃ (10–50 nm in size) (Wu & Li, 2000). The solid reactions between CuO and Cu–14 at.%Al alloy or Cu₉Al₄ inermetallic compound during high energy mechanical milling to produce Cu-Al/Al₂O₃ have been studied (Ying & Zhang, 2003). Arami et al. (Arami et al., 2008) synthesized the Al(Cu)-Al₂O₃ nanocomposite through gradual mechanochemical reaction because of nonstoichiometric composition of
CuO and Al (Al-5.8 wt.%CuO). TEM image and corresponding EDS analysis of Al-CuO powder mixture milled for 60 h is shown in Fig. 9. Nanometric alumina particles, mostly located at the grain boundaries, could be seen in Fig. 9.

 $Al(Ce)-Al_2O_3$ nanocomposite is also fabricated by mechanochemical reaction in Al-CeO powder mixture (Reddy, 2007). Tavoosi et al. have also reported the formation of Al-13.8 wt%Zn-5 vol%Al₂O₃ (Al(Zn)-Al₂O₃) nanocomposite by mechanochemical reaction of Al-ZnO powder mixture followed by hot pressing (Tavoosi et al., 2008), (Tavoosi et al., 2009). The crystallite, relative density, and hardness of hot pressed samples with and without Al₂O₃ at different temperature are presented in Table 3.



Fig. 8. TEM bright field image of 60 h ball milled MoO₃+Al+Cu powder mixture to produce Cu(Mo)-30 Vol.%Al₂O₃ nanocomposite at two magnifications (Sabooni et al., 2010).

Fig. 10 shows the hardness changes of bulk Al–13.8 wt%Zn-5 vol%Al₂O₃ and Al–13.8 wt%Zn vs. annealing time at different temperatures. As can be seen from this figure, the hardness value for Al–13.8 wt%Zn-5 vol%Al₂O₃ after annealing at 200 and 400 C remained constant. However, annealing at 500 C for longer times causes grain growth and therefore a decrease in hardness value. The Al–13.8 wt%Zn-5 vol%Al₂O₃ is more stable than Al–13.8 wt%Zn because of the effect of 5 vol%Al₂O₃ nano-particles in the matrix (Tavoosi et al., 2009).

El-Eskandarany et al. synthesized Fe-MgO by mechanochemical reaction of Fe_2O_3 and Mg (El-Eskandarany et al., 2001). Co-Al₂O₃ nanocomposite is also prepared by mechanochemical reduction of CoO by Al. The average grain sizes of the nanocomposite powders are reported 19 nm for Co and 28 nm for Al₂O₃ after the completion of the reduction reaction (Li et al., 2007). Karimzadeh et al. also reported the synthesis of Zn-Al₂O₃ by mechanochemical reaction between ZnO and Al. The microhardness value of produced nanocomposite powder was about 350HV which was 10–15 times higher than the microhardness of pure zinc (20–30 HV) (Karimzadeh et al., 2008).

Samples	Temperature (°C)	Relative density (%) (S.D. 0.5%)	Hardness (HV)	Crystallite size (nm)
Al-13.8 wt%Zn/5 vol%Al ₂ O ₃	400	95	150	40
	500	99.6	185	40
Al-13.8 wt%Zn	400	96	120	40
	500	99.8	150	40

Table 3. Relative density, hardness and crystallite size of bulk Al-13.8 wt%Zn-5 vol%Al₂O₃ and Al-13.8 wt%Zn (Tavoosi et al., 2009).



Fig. 9. TEM (bright field) image, EDS analysis and SAD pattern of Al-CuO powder mixture after 60 h ball milling (Arami et al., 2008).



Fig. 10. The hardness changes of Al–13.8 wt%Zn-5 vol%Al₂O₃ and Al–13.8 wt%Zn vs. annealing times at different temperatures (Tavoosi et al., 2009).

The presence of metallic particles in ceramics adds physical properties inherent to the metallic phase, such as electric and thermal conductivity or magnetic properties. This combination of properties makes ceramics - metals composite excellent candidates for electric, optic, and magnetic devices or chemical sensors. Some properties such as toughness and wear behavior of ceramic - metal composites are expected to be improved in compare to monolithic ceramic phase (Chalwa, 1993). So, fabrication of ceramic matrix nanocomposite can strongly improve the room temperature toughness and high temperature strength of ceramics (Mishra & Mukherjee, 2001). Matteazzi and Caer synthesized nanometer-sized A1₂O₃-M composite (M= Fe, V, Cr, Mn, Co, Ni, Cu, Zn, Nb, Mo, W, Si) by mechanochemical reaction of an appropriate metal oxide and (Matteazzi & Caer, 1992). Recently, Heidarpour et al. synthesized Al₂O₃-Mo nanocomposite with different volume persent of Mo (Heidarpour et al., 2009). Mostaan et al. also reported for the first time on mechanochemical reaction in Nb₂O₅+Al powder mixture to synthesizing Al₂O₃-Nb nanocomposite (Mostaan et al., 2010a). They investigated the reaction mechanism and activation energy (E_a) of aluminothermic reaction between Al and Nb₂O₅ under nonisothermal conditions using XRD and differential thermal analysis (DTA). It was found that the mechanically milled Al-Nb₂O₅ powder mixture was converted to Al₂O₃-Nb composite in three stages and during the reduction intermediate Nb oxides (NbO₂ and NbO) were formed (Mostaan et al., 2010c).

4.2 Intermetallic-ceramic nanocomposite

Intermetallic compound is an important class of materials because of a combination of its high tensile strength, low density, good wear resistance, and creep resistance. These properties have led to the identification of several potential usages including structural applications and protective coatings (Sauthoff, 1995). Two major problems that restrict the application of Intermetallic are poor low-temperature ductility and inadequate high-temperature creep resistance. These limitations can be overcome by introducing ceramic particles as reinforcements (Morris, 1998). Originally, reinforcement phase can be introduced in the matrix by two routs namely ex-situ addition of reinforcement particles and in-situ formation of reinforcement phase via a displacement reaction which both phase (Intermetallic and ceramic) are formed during ball milling. The later route can be done by mechanochemical process which has an advantage over other fabrication route because of its capability of producing chemical compatible phase as well as nanosized structure with high uniformity. The important Intermetallic compound is NiAl, FeAl, TiAl, and NiTi that mechanochemically synthesized intermetallic-ceramic nanocomposite were overeviewed.

Development of NiAl-Al₂O₃ nanocomposites by mechanical milling has been achieved by the milling of Ni-Al-Al₂O₃ (lin et al., 2000) and NiO-Al powder mixture (Oleszak, 2004), (Anvari et al., 2009), (Udhayabanu et al., 2010). In order to fabricate the Ni₃Al- or NiAlbased composite via mechanochemical displacement reaction, the nickel oxide (NiO) could be used to reduce by aluminum according to the following reactions:

$$3NiO + 3Al \rightarrow Ni_3Al + Al_2O_3$$
 (4)

$$3NiO + 5Al \rightarrow NiAl + Al_2O_3$$
 (5)

The first report on synthesis of NiAl-Al₂O₃ nanocomposite by mechanochemical reaction of stoichiometric 3NiO+5Al powder mixture was reported by Oleszak (Oleszak, 2004). XRD

pattern of 3NiO+5Al powder mixture as-received and after different ball milling time are presented in Fig. 11. XRD pattern of 3NiO+5Al powder mixture as-received and after 1 h milling time show the peaks corresponding the NiO and Al phases whereas the XRD pattern of 1.5 h ball milled sample indicates the formation of NiAl and Al_2O_3 phases. The crystallite size and lattice strain of phases measured from XRD pattern using Williamson-Hall Method were reported in the range of 40-50 nm and 0.4% for 2 h milled and 10-20 nm and 0.9% for 4 h milled samples.

Anvari et al. was investigated the mechanochemical reaction of NiO-38 wt% Al and NiO-34wt% Al-41 wt% Ni in order to give the final product NiAl-Al₂O₃ composite with 40 and 20 vol.% contribution of alumina, respectively (Anvari et al., 2009). They reported that NiAl-40 vol.% Al₂O₃ nanocomposite formed by a combustion reaction. In contrast for NiAl-20 vol.% Al₂O₃ high exothermic reaction did not occur during the milling process, due to the presence of Ni content in initial mixture. Increasing Ni concentration increased the start time of NiAl and Al₂O₃ formation, and changed the morphology of products. XRD patterns of NiO+Al and NiO+Al+Ni powder mixtures as-received and after different milling times are shown in Fig. 12 and 13, respectively. As can be seen, the NiAl and Al₂O₃ phases were synthesized in both samples during milling.



Fig. 11. XRD pattern of 3NiO+5Al powder mixture as-received and after different ball milling time (Oleszak, 2004).

Udhayabanu et al. also synthesized nanocrystalline NiAl based nanocomposite with 30 vol.% of Al₂O₃ by carrying out milling of NiO, Al, and Ni powder mixture in toluene medium for 20 h followed by heating. They reported NiAl phase formation and NiO reduction occur gradually and simultaneously during milling. Small amount of NiO which remains unreacted in 20 h milling got reduced at 420 °C on heating. Small amount of Ni₃Al phase is also formed as intermediate product and it later transforms to NiAl phase above 900 °C on heating. The amorphous alumina is formed as the product of the NiO reduction by Al and it transforms to stable α -Al₂O₃ at 1000 °C via the formation of metastable transition γ -Al₂O₃. The TEM results revealed that the α -Al₂O₃ particles are 11±3 nm in size and the average crystallite size of NiAl phase is 115±40 nm in the 20 h milled powder after heating to 1120 °C.



Fig. 12. XRD patterns of NiO-38 wt% Al powder mixtures as-received and after milling for 0.5 h (Anvari et al., 2009).



Fig. 13. XRD traces of NiO-34 wt% Al-41 wt% Ni powder mixtures as-received and after different milling times (Anvari et al., 2009).

Mousavi et al. reported the Synthesis of NiTi-Al₂O₃ nanocomposite by mechanochemical reaction of a powder mixture containing NiO, Al, Ti and Ni. They also reported the combustion mechanochemical reaction between NiO and Al leading to the formation of nanocomposite for this dialued system in presence of Ni and Ti (Mousavi et al., 2009).

Iron aluminides compound, especially FeAl and Fe₃Al compounds, possess a combination of attractive physical, thermal and mechanical properties including low density, high tensile strength, good oxidation, corrosion, and sulfidation resistance. These properties along with low cost make iron aluminides potentially useful for structural and coating applications (Sauthoff, 1995). Incorporation of ceramic reinforcement in iron aluminides lead to enhance the high temperature strength (Subramanaian et al., 1997), (Subramanaian et al., 1998) as well as wear resistance of iron aluminides (Alman et al., 2001). Oleszak and Krasnowski synthesized FeAl-Al₂O₃ nanocomposite by mechanochemical reaction of Fe₂O₃+4Al powder mixture (Oleszak & Krasnowski, 2001). They reported the average crystallite size of 10 nm after ball milling and 40-50 nm after subsequent annealing. Khodaei et al. investigated the mechanochemical synthesis of Fe₃Al-Al₂O₃ with different vol.% of Al₂O₃ (Khodaei et al., 2008), (Khodaei et al., 2009a), (Khodaei et al., 2009b). The thermodynamic consideration based on the theoretical adiabatic temperature, T_{ad} , associated with different reactions between Fe₂O₃, Al, and Fe, has revealed the modality of the mechanochemical reaction. Fe₃Al-Al₂O₃ nanocomposite powder containing 57vol. % Al₂O₃ was synthesized by mechanochemical combustion reaction of 3Fe₂O₃+8Al powder mixture. Combustion reaction in this system is detected by abrupt increase in vial temperature (Khodaei et al., 2009a). The combustion is also observed by opening of vial at the expected time. Fig. 14 shows the opened vial during the combustion reaction.



Fig. 14. Images of opened vial during combustion reaction of 3Fe₂O₃+8Al powder mixture.

The XRD patterns of $3Fe_2O_3 + 8Al$ powder mixture as-received and after different milling times are shown in Fig. 15. XRD patterns of powder mixture after 2 h of milling time (prior to combustion reaction) was identified as a mixture of Fe_2O_3 and Al with nanocrystalline structure. XRD patterns immediately after combustion, Fig. 15(c), showed no Fe_2O_3 and Al peaks. The diffraction lines of reaction products were identified as Al_2O_3 and Fe_3Al intermetallic compound. The results showed successfully synthesized Fe_3Al and Al_2O_3 by mechanochemical reaction of $3Fe_2O_3 + 8Al$ powder mixture. In contrast, Fan et al. reported that during reaction of Fe_2O_3 and molten aluminum in $3Fe_2O_3 + 8Al$ system, instead of thermodynamically predicted Fe_3Al intermetallic compound, FeAl₂O₄ predominately forms

(Fan et al., 2006). In order to study the distribution of phases and microstructure of Fe₃Al-Al₂O₃ nanocomposite, the produced powder after 20 h of milling time was cold pressed and then sintered at 1400 °C for 1 h. Cross-sectional micrograph of sintered specimen is shown in Fig. 16. As seen, the distribution of Fe₃Al and Al₂O₃ phases is homogeneous.



Fig. 15. XRD patterns of 3Fe₂O₃ + 8Al powder mixture as-received and after different milling times (Khodaei et al., 2009a).

This ultrafine (>2µ) and uniform microstructure of metallic-ceramic phases without "corerim" feature is resulted from ball milling process (Khodaei et al., 2009a). Khodaei et al. also synthesized Fe₃Al-30 vol.% Al₂O₃ nanocomposite by addition of Fe to Fe₂O₃+Al powder mixture. The modality of mechanochemical reaction of Fe₂O₃+Al+Fe powder mixture is determined by calculating the Tad of reaction as a gradual way (Khodaei et al., 2009b). For comparison, the Fe₃Al-30 vol.% Al₂O₃ nanocomposite was also prepared by ex situ addition of Al₂O₃ nanopowder to Fe-Al powder mixture followed by ball milling. The Fe₃Al-30 vol.% Al₂O₃ powders prepared by these two routes were consolidated in order to study the microstructure as well as mechanical properties of the samples. Cross-sectional SEM micrographs of the sintered samples are shown in Fig. 17. The distribution of Fe₃Al and Al₂O₃ phases in ex situ added Al₂O₃ sample is not homogeneous whereas for mechanochemically synthesized sample which involved in situ formation of Al₂O₃, a distribution of Al_2O_3 is achieved. Moreover, the microstructure uniform of mechanochemically synthesized sample is finer than that obtained for ex situ added Al₂O₃ sample and contains lower amount of porosity (Khodaei et al., 2009b). Subramanian et al. synthesized the Fe₃Al-20 vol.% Al₂O₃ composite via reactive sintering of Fe₂O₃ and FeAl powder mixture by pressureless sintering (Subramanian et al., 1997) and hot pressing (Subramanian et al., 1998) had a foam-type feature in which the Al_2O_3 phase are formed as rings around the Fe₃Al matrix (Fig. 18), probably from a reaction of FeAl and Fe₂O₃ located along the grain boundaries. These results show that the microstructure of Fe₃Al-Al₂O₃ composite produced by mechanochemical process has better characteristics compared to other processing routes. Evaluation of the mechanical properties of consolidated samples included the determination of hardness and fracture stress by three-point flexure testing at room temperature. These values for mechanochemically synthesized and ex situ added Al₂O₃ samples produced by Khodaei et al. compared with reactive sintered samples produced by Subramanian et al. are given in Table 4. As can be seen, the hardness and fracture strength values of mechanochemically synthesized nanocomposite are higher than those produced by other methods.



Fig. 16. SEM cross-sectional microstructure of consolidated Fe₃Al– 57 vol.% Al₂O₃ nanocomposite powder prepared by mechanochemical reaction (Khodaei et al., 2009a).



Fig. 17. SEM cross-sectional microstructure of consolidated Fe₃Al– 30 vol.% Al₂O₃ nanocomposite powder prepared by: (a) mechanochemically synthesized (b) ex situ added Al₂O₃ followed by ball milling. (Khodaei et al., 2009b).



Fig. 18. SEM micrographs of an Fe₃Al-20 vol.% Al₂O₃ processed by an in situ displacement reaction via reactive sintering (Subramanian et al., 1998).

Composition	Fabrication route of Al ₂ O ₃	Hardness (Hv)	Fracture stress (MPa)
Fe ₃ Al-30 vol.% Al ₂ O ₃	Mechanochemical	538 ± 20	173±9
Fe ₃ Al	-	378 ± 19	Not tested
Fe ₃ Al-20 vol.% Al ₂ O ₃ Fe ₃ Al-20 vol.% Al ₂ O ₃	Reactive sintering Reactive sintering	222^{a} 355 ± 30	107^{a} 184±2
Fe ₃ Al		308 ± 5	896 ^a

Table 4. Vicker's hardness and room temperature three-point fracture stress of Fe₃Al-Al₂O₃ samples prepared by different routs (Khodaei et al., 2009b).

Rafiei et al. (Rafiei et al., 2009) reported the synthesizing (Fe,Ti)₃Al–Al₂O₃ nanocomposite by mechanochemical reaction in Fe+Al+TiO₂ powder mixture. Addition of third alloying element such as Ti and Cr to Fe₃Al intermetallic compound can lead to the improvement of mechanical properties. They found that the TiO₂ is gradually reduced by Al during milling. This reaction led to the formation of crystalline Ti and amorphous Al₂O₃. On further milling Ti (reduced from TiO₂) and remaining Al dissolved into Fe lattice and formed a Fe(Al,Ti) solid solution which transformed to (Fe,Ti)₃Al intermetallic compound with disordered DO3 structure at longer milling times. Annealing of final structure led to the crystallization of amorphous Al₂O₃ and ordering of (Fe,Ti)₃Al matrix.

Forouzanmehr et al. (Forouzanmehr et al., 2009) reported the synthesis TiAl-Al₂O₃ nanocomposite by mechanochemical reaction of TiO₂ and Al and subsequent annealing. They found that titanium oxide is gradually reduced by Al during milling. The Al(Ti) solid solution formed at the early stage of milling. Diffusion of Ti into Al is found to be dominant process. Fig. 19 shows TEM micrographs and SAD pattern of the powder milled for 60 h followed by annealing at 900°C. Fig. 19(a) displays the bright field micrograph and Fig. 19(b) shows dark field micrograph indicating nano-sized phases with less than 50 nm. The SAD pattern, Fig. 19(c), also indicates fine crystalline size as well as the absence of preferred orientation. They also reported the good agreement regarding the grain size of the phases estimated from TEM observation and that from XRD analysis using Williamson-Hall method.

Zakeri et al. for the first time reported the mechanochemically synthesized MoSi2–Al2O3 nanocomposite by ball milling of mixture of MoO3, SiO2 and Al powder (Zakeri et al., 2007). They found that this reaction proceeds trough the combustion mechanochemical reaction. NbAl₃–Al₂O₃ nanocomposite powder with 40 vol.% Al₂O₃ was also directly synthesized by Mostaan et al. (Mostaan et al., 2010b) using mechanochemical reaction between Nb₂O₅ and Al powders. Measurement of vial temperature, XRD analysis, and morphology changes during ball milling confirmed the occurrence of combustion reaction which led to the formation of NbAl₃ intermetallic compound and Al₂O₃ phase. Thermal behavior results showed that nanocomposite powders were stable during heating. XRD pattern of Nb₂O₅ and Al powder mixture as-recievd and after different milling time are shown in Fig. 20.



Fig. 19. TEM micrographs of TiAl-Al₂O₃ nanocomposite powder produced by milling of TiO₂+Al for 60 h followed by annealing at 900 °C: (a) Bright field, (b) Dark field, and (C) SAD pattern (Forouzanmehr et al., 2009).



Fig. 20. XRD pattern of Nb_2O_5 and Al powder mixture as-recieved and after different milling times (Mostaan et al., 2010b)

5. Conclusion

The mechanochemical processing is a technique that could be used to synthesize composite structure which has an advantage over other fabrication route because of its capability of producing chemical compatible phase as well as nanosized structure with high uniformity. These advantages provide a useful technique for preparation of nanocomposite powder used in fabrication of advanced engineering parts trough powder metallurgy methods. The future works in this area should be done in utilizing the advanced powder metallurgy methods for consolidation of mechanochemically synthesized nanocomposite powders.

6. References

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Synthesis of Hydroxyapatite/Collagen Bone-Like Nanocomposite and Its Biological Reactions

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1. Introduction

Bone is a typical nanocomposite of inorganic and organic substances mainly composed of nanocrystals of hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$, HAp) with nonstoichiometry 20-40 nm in length and type-I collagen molecules 300 nm in length. In microscopic observation of bone, collagen molecules are covered with HAp nanocrystals, and they form nanocomposite fibers in which HAp *c*-axes are approximately aligned along with collagen molecules (Bacon et al., 1979, Sasaki & Sudoh, 1997). Bone has two important roles in vertebrates; one is as a structural material to maintain vertebrates body structure and to guard important internal organs, such as brain, heart and lung, and another is as an organ to control calcium ion homeostasis by resorbing bone mineral according to deficiency of calcium ion. These two roles are kind of antinomical properties as industrial materials, i.e., TOUGH to endure to external forces for whole life and BREAKABLE to allow calcium release by bone cell functions on demand. However, change our viewpoint about toughness of material, solution of the antinomy is concluded to one property. That is, every materials fatigue by long time use; thus, periodic renewal of material is necessary to maintain enough toughness of bone for whole life. Thus, bone has to be renewed easily by cell functions. That is almost the same meaning as a breakable property of bone. Accordingly, requirement of bone can be translated as follows; bone has to be decomposed by cell functions but be stable without them.

Fortunately, our ancestors needed to preserve calcium and phosphate ions in their body when they left from sea. Calcium and phosphate easily form insoluble compound in aqueous solution, brushite (CaHPO₄•2H₂O), octacalcium phoshate (Ca₈H₂(PO₄)₆•5H₂O) and HAp, and all calcium phosphates are changed into HAp in aqueous or moistured condition, because it is most stable compound in these conditions. Further, HAp formed in regular

biological condition is a nanocrystal. Our ancestors, as a result, preserve HAp in endoskelton as a calcium and phosphate reservoir. Collagen had been developed in evolutional process as a structural organic molecule and chosen as main organic component of endoskelton. Accumulation of HAp in endoskelton and following well-aligned nanostructure of HAp and collagen produced highly hardness and elasticity of bone to barely endure to external force in short period. In addition, HAp is very stable in neutral pH condition but unstable in acidic and basic conditions, and collagen is a protein and can be decomposed by appropriate enzymes. Thus, bone is stable in our body and become unstable when cells release proton and enzyme.

Some readers wondering why HAp ceramics, sold as artificial bones and fillers, are considered as a non-resorbable material even with the same chemical properties as bone HAp. One reason is difference in chemical composition. Bone HAp contains large amount of carbonates due to high amount of carbonate ion concentration in our body fluid. Carbonate ion increases HAp solubility and inhibits HAp crystal growth. Another and much important reason is size of HAp. Generally, HAp sintered bodies including pillar and wall of porous HAp ceramics is dense, and crysyal size of HAp in them is approximately 1 μ m. In this dense and large crystal size, HAp needs significantly longer period to be decomposed by cell functions in comparison to HAp nanocrystals dispersed in collagen molecules because of difference in surface area.

According to these considerations, mimicking of bone nanostructure can be a solution of problems existing in present artificial bone filler materials.

2. Synthesis of HAp/Col bone-like nanocomposite

2.1 Bone remodeling process

Bone remodeling process is a regular bone metanbolism regulated by cells aiming to maitain machanical strength of bone and Ca ion homeostatis in body fluid and constantly repeated in our bone to achieve the former aim. This regular bone remodeling is carried out by coupling of an osteoclast and an osteoblast. The osteoclast is one of a multinucleated giant cell forms through the fusion of mononuclear precorsors, hemopoietic progenitors and resorbs bone by controlling biochemical condition of target site, lowering pH to 3-4 to dissolve HAp and releasing enzyme to decompose collagen. This bone-resorbed site is called "Howship's lacunae." The osteoblasts are accumulated to the Howship's lacunae to form new bone. The formation of bone is simplified as follows:

- 1. The osteoblasts release collagen molecules and they form fibers.
- 2. Calcium phosphate nanocrystals, generally considered as brushite, are supplied from matrix vesicle synthesized by the osteoblasts.
- 3. Hydroxyapatite nanocrystals epitaxially grow on collagen molecules (with some support of calcium phosphates released from matrix vesicles.)

In fact, bone nanostructure formation mechanism have not completely understood yet; however, orientation between HAp nanocrystals and collegen fibers cannot be well explained without some kinds of epitaxy because of its extremely small scale for cells. Thus, functions of cells to form the nanostructure is assumed to be supply of raw materials and adijustment of surrounding condition, at least initial stage, i.e., formation of collagen fibers and formation of HAp nuclei on collagen. These cell functions can be technologically mimicked.

2.2 Processes for mimicking bone formation

Prior to explain our method, several approaches to prepare composite of HAp and collagen are introduced.

First trial to prepare the composite is just mixing HAp or related calcium phosphates in collagen sol and freeze-dry it after gellation of collagen sol (e.g., TenHisen et al, 1995). This method is very simple but difficult to prepare homogeneus composite in which HAp amount is similar to bone (70mass%). Further, this method does not form bone-like nanostructure. So, biological reaction to the composite obtained from this method is just a combination of implantation of collagen sponges and HAp particles.

Second trial is precipitation of HAp nanocrystals on collagen fibers in its sponge or membrane(e.g., Tampieri et al., 2003). This method allows orientaion of HAp and collagen fibers at only low HAp amount. Further, HAp nanocrystals completely cover collagen fibers. This is microcomposite in a sense, i.e., primary components, HAp and collagen, are nano-size but their secondary components are HAp microsized layer and collagen microsized fibers. Accordingly, initial biological reaction is similar to HAp and suddenly changed into reaction to collagen sponge.

Third trial is to mimic bone nanostructure. Polymer induced liquid precursor method allows to synthesis bone-like nanocomposite with almost similar process of bone formation (Olszta et al., 2007). Coprecipitaion of collagen fibers and HAp from thin mixture solution of collagen and calcium phosphate allows nano to milimeter level bone-mimicking structure (Nassif et al., 2010). Both methods assumed to need long period to form HAp on collagen fibers (\geq 1 weeks) and not suit for mass production. Further, the latter paper have not confirm the orientation of HAp and collagen in bone-like HAp content.

Our simultaneous titration method is very simple coprecipitation method to allow selforganization of HAp and collagen (Kikuchi et al., 2001). This method can easily synthesis bone-like oriented HAp/collagen (HAp/Col) composite with high HAp amount even greater than bone (\geq 80mass%). Further, length of the bone-like composite is up to 75 mm at HAp/collagen mass ratio of 3/2 (Kikuchi et al., 2003). Accordingly, this method is considerablly better for mass production which make the HAp/Col composite available to use in practical medicine. The method in details is explained in the followings section.

2.3 Simultaneous titration method

Calcium hydroxide is synthesized by hydration of CaO obtained by burning of CaCO₃ (alkaline analysis grade, Wako Pure Chemical, Japan) to ignore influence of minor elements, Mg and Sr. Schematic drawing of synthesis apparatus is shown in Fig. 1. Aqueous suspension of Ca(OH)₂ and aqueous solution of H₃PO₄ (Regent grade, Wako Pure Chemical, Japan) which contains porcin dermal type-I atelocollagen (Biomedical grade, Nitta Gelatin, Japan) are simultaneously added into a reaction vessel through tube pumps. The HAp/Col forms almost ideally, thus HAp/Col mass ratio and amount obtained are expected by amounts and concentrations of starting materials. composite Pure water is added in the reaction vessel beforehand to allow measuring pH. The pumps are turned on and off by pH meter with power control unit to maintain pH at 9 in the reaction vessel. The reaction vessel is placed in water bath to maitain reaction temperature to 40 °C. The pH 9 is very important because isoelectric point of the collagen exists in pH 7 to 9, and HAp is stably formed by simultaneous titlation of Ca(OH)₂ and H₃PO₄ around pH 9. Temperature is also important to allow collagen fiber formation. Temperature up to 40 °C allows competitive reaction of collagen fiber formation and collegen degeneration. At more than 40 °C, degenetaion of

collagen become dominant reaction and at lower temperature allows to degenerate collagen to gelatin due to delaying of collagen fibril formation at low ionic concentration as in the present reaction. Figure 2 shows transmission electron micrographs of the HAp/Col composite at HAp/Col mass ratio of 4/1. The HAp/Col composite in this photo is approximately 30 μ m in length, and selected area electron diffraction from the HAp/Col composite shows orientation of HAp nanocrystals along with collagen fiber.



Fig. 1. Schematic drawing of synthesis apparatus for HAp/Col bone-like nanocomposite.



Fig. 2. Transmission electron micrograph and selected area electron diffraction of HAp/Col bone-like nanocomposite.

In addition, HAp formation on collagen molecules is supposed to promote collagen fiber formation (Kikuchi et al., 2003). Therefore, concentrations of starting materials in the reaction vessel control fiber length of the HAp/Col composite. Longer fibers are obtained from thinner solution and low HAp/Col ratio. To control the HAp/Col fiber length, starting materials concentrations, their amounts and amount of H₂O previously added in the reaction vessel are controlled as shown in Table 1. Figure 3 shows that the HAp/Col fibers are grown with decreasing of starting material concentration. In fact, most important concentration is Ca, P and collagen concentrations in the reaction vessel. Calcium concentration in the reaction vessel measured with Ca ion electrode shown in Fig. 4 demonstrates that changes in Ca ion concentration in the reaction vessel for low starting material concentrations is more steady than high starting material concentration. Further, presence of collagen molecules also stabilize Ca concentration change at the same Ca and PO₄ concentration. These results suggest that stable and slow HAp heterogenous and epitaxial nucleation on the collagen molecules occurs under low starting material concentration in the reaction vessel. On the contrary, higher starting material concentration rapidly increases Ca and PO4 ion concetrations and allows homogeneous nucleation of HAp in the solution like HAp formation in non-collagen system as well as a heterogenous nucleation on the collagen.

Ca(OH) ₂	Concentration / mM	50	100	200	400	
	Amount / ml	1600	800	400	200	
H ₃ PO ₄	Concentration / mM	15	30	60	120	
	Amount / ml	3200	1600	800	400	
Total Ca/P ratio		1.67 (stoicheometric for HAp)				
Collagen / g		2.01				
H ₂ O in reaction vessel / ml		1600	800	400	200	
HAp/Col mass ratio		4/1				

Table 1. Concentration and amount of starting materials for controlling fiber length of HAp/Col bone-like nanocomposite.



Fig. 3. Photographs of HAp/Col bone-like nonocomposite fibers increasing their length with decreasing in starting material concentrations.



Fig. 4. Changes in calcium concentration in reaction vessel. Fluctuation of concentration decreases with decreasing in concentration or presence of collagen.

2.4 Preparation of artificial bone

Several forms of artificial bone can be prepared from the HAp/Col nanocomposite fibers.

A dense body is prepared by compaction of the HAp/Col with uniaxial and/or cold isostatic pressing methods. The HAp/Col dense body demonstrates maximum 3-point bending strength of 39.5±0.9 MPa and maximum Young's modulus of 2.54±0.38 GPa. These values are 1/5 of cortical bone but higher than those of cancellous bone (Kikuchi et al., 2001).

A paper-like membrane is prepared by filtration of the HAp/Col fibers followed by pressing as shown in Fig. 5 (Kikuchi, 2007). The membrane is easily deform as a wavy membrane as in Fig. 6 (Kikuchi, 2008).



Fig. 5. Flexible membrane prepared from HAp/Col bone-like nanocomposite fibers.



Fig. 6. Wavy membrane prepared from HAp/Col flexible membrane.

A porous body is prepared by lyophylization of the frozen HAp/Col suspension. The HAp/Col fibers, collagen solution, phosphate buffered saline are mixed homogeneously and frozen to grow ices in the mixture. After the freezing, the mixture is lyophylized to remove ices as pores. Collagen molecules in the porous HAp/Col obtained are crosslinked to decrease resorption rate (Kikuchi et al., 2004a). The porous HAp/Col demonstrates sponge-like visco-elasticity as shown in Fig. 7 (Kikuchi et al, 2004b). When the HAp/Col mixture is frozen from one side, unidirectional ice growth creat unidirectional porous structure instead of random pores (Yunoki et al, 2006). Another way to prepare unidirectional porous body is rolling-up the wavy membrane as shown in Fig. 8(Kikuchi, 2008).

3. Biological reactions

3.1 Regeneration of bone defect

All animal tests described in this section are accepted by Tokyo Medical and Dental University Institutional Animal Care and Use Committee. The cylindrical dense HAp/Col with central hole and satellite holes as shown in Fig. 9 were implanted into segmental defect of beagle's tibia 20 mm in length. This size of defect never regenerate without support of



Fig. 7. Viscoelastic porous body prepared from HAp/Col bone-like nanocomposite.



Fig. 8. Unidirectional porous HAp/Col bone-like nanocomposite.



Fig. 9. Dense HAp/Col bone-like nanocomposite with central and satellite holes.

autologous bone transplantation or other material implantation. After 12 weeks of implantation of the HAp/Col, the HAp/Col cannot be detected with X-ray photo. Nakedeye observation of the host site shows no HAp/Col presence and complete regeneration of bone (Fig. 10a). From the histological observation shown in Fig. 10b, rengenerated bone is still young but completely regular bone. Multinucleated giant cells are attached on the surface of the HAp/Col debris found in the new bone tissue. The cells are tartarate-resistant acid phosphatase positive. Thus, the cells are identified as osteoclasts. Spindle-shaped cells are attached on the opposite side of the HAp/Col with non matured tissue between. These cells are alkaline phoshatase (AlkP) positive and identified as osteobasts. These results mean that the HAp/Col is resorbed by the osteoclasts followed by new bone formation by the osteoblasts. This osteoclast-osteoblast coupling is completely the same as the bone remodeling process, especially as the same reaction when autologous bone is transplanted. That is, the HAp/Col is incorporated into bone remadeling process (Kikuchi et al., 2001). In fact, this is the first evidence of incorporation of the HAp/Col into bone remodeling process and the world first reported material that completely incorporated into bone remodeling process. The HAp/Col porous body also revealed the same biological reaction when it is implanted into a hole of rabbit's tibia (Tsuchiya et al., 2008). Accoring to the results, enough pore size and well interconnected porous structure to allow cell and tissue migration was important for good bone regeneration. Recently, importance of pore structure in critical bone defect regeneration has been being investigated using series of unidirectional porous HAp/Cols (Aoki et al., 2009). Further, effects of combination of cytokine and the HAp/Col were investigated. The HAp/Col is a good carrier of recombinant human bone morphogenetic protein-2 (Itoh et al., 2001) and regenerates large osteochondral defect with small amount of basic fibroblast growth factor (Maehara et al., 2010).



Fig. 10. Naked-eye (a) and histological (b) observations of dense HAp/Col bone-like nanocomposite after 12 weeks' implanted into segmental defect of beagle's tibia.

3.2 Cell reactions in vitro

Influence of osteogenic activity of the HAp/Col was examined by three-dimensional culture with pressure/perfusion on the porous HAp/Col (Yoshida et al., 2010). Human osteoblastlike cells, MG-63, were seeded to the HAp/Col sponge and cultured for 24 hour in static condition to allow secure attachment of cells on the wall of HAp/Col sponge. Then, the cellseeded HAp/Col sponge was transferred into pressure-proof culture column. The cells were cultured in the column in growth medium (Dulbecco's modified Eagle's medium supplemented with 10% (v/v) fetal bovine serum, 100 U/ml penicillin and 100 μ g/ml streptomycin) for 6 day with medium perfusion at 1.3 ml/min to allow cell proliferation into the sponge. After 6 days' incubation, the medium was changed into osteogenic medium (growth medium supplemented with 50 μ g/ml L-ascorbic acid phosphate magnesium salt and 10 mM β -glycerophosphate). In addition, static pressure at 3.2 MPa was applied with a back-pressure regulator with 1.3 ml/min perfusion. The medium was stocked in the reservoir and changed every 3 days. Conventional collagen sponge was used as a control. In the first 10 days, no significant difference in cell proliferation estimated from total DNA amount is found between cells on the HAp/Col and collagen sponges; however, the cells on the HAp/Col sponge demonstrates significant higher proliferation against the cells on the collagen sponge. On the contrary, AlkP gene expressions, one of osteogenic markers, of the cells on the collagen sponge at day 7 and 10 are significantly greater than those of the cells

on the HAp/Col sponges. Other osteogenic marker, osteocalcin, gene expression shows no significant difference between them. The reason of these phenomena is explained by histological and scanning electron microscopic observations. Histological sections at day 21 shown in Fig. 11 demonstrate that both sponge are covered with cell layers (Fig. 11a and 11b); however, many cells migrate into the center of HAp/Col sponge (Fig. 11c)and very few cells migrate into the center of collagen sponge (Fig. 11d). The AlkP gene expression of osteoblastic cells requires certain numbers of cells and their junction by their accumulation. On the collagen sponge, this accumulation is easily achieved by cell proliferation only on its surface and continued up to the end of experimental period. Contrarily, cell proliferation on the HAp/Col sponge promotes not only on the surface but in the HAp/Col sponge along with its pore walls. These differences in cell proliferation manners explain that higher AlkP activity on the collagen sponge at early stages without significant difference of cell proliferation on both sponges as well as significant higher cell numbers (total DNA amounts) for the HAp/Col sponge. Another significant difference is an extracellular matrix (ECM). The ECM from cells on the collagen sponge has no calcium phosphates but that from the cells on the HAp/Col sponge contains calcium phosphates as shown in Fig. 12. These results suggest the HAp/Col sponge is expected to be a good scaffold for bone tissue regeneration as well as a bone filler material.

Further, enhancement of osteogenic activity of MG63 cells is confirmed under twodimensional culture on the HAp/Col membrane (Kikuchi, 2007). Cells grow very well on the membrane and become confluent in 7 days as the same as the cells on conventional tissue culture polystyrene (TCPS) well as shown in Fig. 13. The cells on the HAp/Col



Fig. 11. Hematoxylin and eosin stained histological section of HAp/Col (a: periphery, c: center) and collagen (b: periphery, d: center) sponge at day 21.



Fig. 12. Scanning electron micrographs of cells on HAp/Col sponge (a) and collagen sponge (b). Both cells secreted extracellular matrices (ECM); however, calcium phosphates only formed on ECM secreted by cells on HAp/Col as shown in inlet chart.



Fig. 13. Phase contrast micrographs of MG63 cells on HAp/Col membrane (a) and tissue culture polystyrene (b) at 7 days.

membrane were observed with a conventional translucent phase contrast microscope, thus image is not clear as the TCPS but enough to observe cell morphology. Alkaline phosphatase gene expression of the cells on the HAp/Col membrane is 3.5 times greater than that on TCPS when cells culture without the osteogenic supplements. When the cells culture with the supplements, AlkP gene expression on the HAp/Col is 3.2 times greater than that on the TCPS. That is, the HAp/Col is expected to be a good scaffold for osteoblast culture for bone regenerative medicine.

In addition, mouse primary bone marrow cells cocultured with mouse primary osteoblasts differentiate into osteoclast without adding of any differentiation promoting supplements as shown in Fig. 14 (Kikuchi & Irie, 2009). The mechanism of differentiation led by the HAp/Col is still under investigation, but the HAp/Col may affect osteoblast's activities to release some signals for osteoclast differentiation as well as to activate osteogenic activity.



Fig. 14. Photographs of tartrate-resistant acid phosphatase stained specimens after coculture of mouse osteoblasts and bone marrow cells. Osteoclasts differentiated from bone marrow cells exist at red-stained parts.

4. Conclusion

Bone nanostructure is reproduced by simple simultaneous titration method with maintaining pH and temperature suit for self-organization by controlled HAp nanocrystal formation on collagen molecules. This result is supportive for reproduction of biominerals with control of starting materials, their concentration and surrounding conditions for biomineral formation. As an artificial bone material, the HAp/Col bone-like nanocomposite is a promising material due to its excellent bioactivity, biocompatibility, formability, cytocompatibility and viscoelastic property. In addition, the HAp/Col is also beneficial as a cell scaffold.

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Structure-Gas Transport Property Relationships of Poly(dimethylsiloxane-urethane) Nanocomposite Membranes

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1. Introduction

Hybrid organic-inorganic materials based on incorporation of polyoctahedral oligomeric silsesquioxanes (POSS) into polymeric matrices have received a considerable attention (Gnanasekaran et al, 2009; Krishnan et al, 2005; Chang et al, 2003; Phillips et al, 2004; Kudo et al, 2006; Hong, 1997; Isayev et al, 2004; Ni et al, 2004). Silsesquioxane (Fig. 1) (Laine et al, 2005) consists of a rigid, crystalline and silica-like core structure.



Fig. 1. Silsesquioxanes. (a) Q8 (Q = SiO_{2/2}); R =H, vinyl, epoxy, methacrylate, etc. (b) R_8T_8 (T = R-SiO_{3/2}); R = alkyl, alkene, acetylene, acrylate, (c) Typical sizes/volumes.

POSS derivatives have two unique features: 1) Their chemical composition (RSiO_{1.5}) was found to be intermediate between that of silica (SiO₂) and siloxane (R₂SiO). 2) POSS compounds can be tailored to have various functional groups or solubilizing substituents that can be attached to the POSS skeleton. POSS molecule was perfectly defined spatially (0.5-0.7 nm), have general formula (RSiO_{1.5})_{*a*}(H₂O)_{0.5*b*}, where R is a hydrogen atom or an organic group and *a* and *b* are integer numbers (a = 1, 2, 3, ...; b = 0, 1, 2, 3, ...), with a + b =2*n*, where *n* is an integer (n=1, 2, 3, ...) and $b \le a + 2$. Of several structures of silsesquioxanes (random, ladder and cage), cage structure contains 8 silicon atoms placed at cube vertices. Cubic structural compounds (completely and incompletely condensed silsesquioxanes) are commonly illustrated as T₆, T₇, T₈, T₁₀ and T₁₂ based on the number of silicon atoms present in cubic structure (Fig. 2). POSS based compounds were thermally and chemically more stable than siloxanes. A variety of POSS nanostructured chemicals contain one or more covalently bonded reactive functionalities that are suitable for polymerization, grafting, surface bonding, or other transformations (Lichtenhan et al, 1999; Lichtenhan et al, 2001). Incorporation of nanosized POSS macromers into polymers have produced significant property enhancements in processability, toughness, thermal and oxidative resistance as well as reduction in flammability and increased gas permeability.



Fig. 2. Chemical Structures of different types of silsesquioxanes

1.1 Classification of silsesquioxanes

The chemistry of silsesquioxanes were classified into three broad groups on the basis of functional groups

1.1.1 Mono-functional silsesquioxanes:

These are suitable POSS monomers for the synthesis of linear thermoplastic nanocomopsites. Prepared by the selective hydrolysis of alkyl or aromatic trichlorosilane with water followed by *in situ* reaction with R'SiCl₃ (R' = functional group). Corner capping reaction yields a closed cube with 7 corners of inert groups (cyclopentyl or cyclohexyl) and the remaining one vertex possesses highly reactive functional group such as amine (Haddad and Lichtenhan, 1996), styryl (Ikeda and Saito, 2007) acrylic (Zhang, 2009), epoxide (Liu and Zheng, 2006), norbornyl (Zheng et al, 2001) and bisphenol (Iyer and Schiraldi, 2007) (Fig. 3).



Fig. 3. Synthesis and structures of monofunctional POSS macromonomers

1.1.2 Multifunctional monomers

These are prepared by hydrosilylation reaction using Pt catalyst with either *m*-isopropenyl- α - α '-dimethylbenzyl isocyanate or 2-chloroethyl vinylether or allyl alcohol or 4-acetoxystyrene or 4-[(2-(vinyloxy)ethoxy)methyl]cyclohex-1-ene (Fig. 4).



Fig. 4. Synthesis of octafunctional POSS macromonomers through hydrosilylation reaction

1.1.3 Incomplete silsesquioxanes

Heptameric siloxanes with partially formed cages containing 2 or 3 residual silicon hydroxyl functional groups, obtained through hydrolysis/condensation of alkyl- or aryl trichlorosilanes, are called as incomplete silsesquioxanes. A variety of NCs were obtained through reactive silicon hydroxyl functional groups(-SiOH) (Fig. 5).



Fig. 5. Synthesis of polynorbornene, polyurethane and cyanate ester nanocomposites using partially caged silsesquioxanes.

1.2 Preparation of membranes – literature reports

Organic–inorganic hybrid membranes could be prepared by simply embedding the inorganic particles such as silica, TiO₂, ZrO₂ alumina, and carbon molecular sieves (Peinemann et al, 2005; Yave et al, 2007; Genne et al, 1997; Wara, 1995; Miller, 2003). In particular the incorporation of nanosized inorganic particles in the membranes is of more interesting in the gas separations. The main disadvantage of incorporating fillers to the polymers by blending is the agglomeration of particles and formation of nonselective voids at the interface of particles and the polymer matrix. The formation of voids between both materials could be controlled through *in situ* generation of inorganic nanoparticles in the polymer matrix through sol–gel process or crosslinking the functional group of nanoparticle with polymer functional groups (Nunes, 1999; Park, 2003). Therefore, the modification of

fillers and matrices has become an expanding field of research as the introduction of functional groups can improve dispersion of fillers and change chemical affinities of penetrants in nanocomposite membranes. There is much scope for research innovation and the development of polymer-inorganic nanocomposite membranes for gas separation.

1.3 Importance of membrane technology

Natural gas plays an important role in today's energy production and is one of the fastest growing fossil fuels. It has been widely used as the energy source for electricity generation as well as the natural gas powered vehicles domestic appliances, manufacturing of metals and chemicals. According to the available statistics that US produces 50% of this domestic comsumption of electricity through the combustion of natural gas. There is energy possibility that the dramatic increase use of natural gas in the next 20-30 years. This main reason being that the natural gas offers many environmentally friendly properties without producing sulphur oxides (SOx), low levels of nitrogen oxides (NOx) and relatively lower emissions of carbon dioxide than those of other fossil fuels such as coal and oil. CO_2 is a major component contributing to the sweetening of natural gas and causing greenhouse effect. Therefore, the separation of CO_2 from natural gas is utmost important as this may dramatically reduce the pipeline corrosions and enhance the efficiency of high-purity energy products (Paul and Yampol'skii, 1994; Table-Mohammadi, 1999; Li et al, 2007). According to acceptable pipeline requirements for optimizing corrosion, the concentration specification of CO_2 must be <2%. Amine absorption is a main strategy that is currently employed in the industry to facilitate CO₂ removal from natural gas (Yeh and Pennline, 2001). In contrast, membrane separation processes have been proven to be technically and economically far superior in view of their versatile properties, simplicity and ease of installation and operation, low maintenance requirements and reduced cost.

1.4 Structure – property relationships

1.4.1 Morphology effect on permeability:

Generally, surface morphology of memebranes depend on polymer molecular structure, composition, molecular weight, and can also be influenced by a suitable choice of the substrate surface free energy. The POSS portion combines the features of organosilicon compounds and possess low free energy (Youngblood and McCarthy, 1999). Thus, the enrichment of the POSS portion at the surface could occur upon incorporating the organic-inorganic amphiphile into organic polymer and the surface hydrophobicity of materials will significantly be enhanced (Koh, 2005). Hence, the hydrophobic part of POSS was chosen to study the effect of POSS on surface morphology of polymers and thereby influencing the permeability and selectivity of gases.

1.4.2 Incorporation of PU/PI on mechanical properties of PDMS:

Polydimethylsiloxane (PDMS) ($\overline{M_n}$ =5,600) has the highest gas permeability of all synthetic polymers produced so far on an industrial scale, except for some glassy polymers with a high free volume fraction. However, it has poor separation ability for small gas molecules (eg., O_2 , N_2 , H_2 and CO_2), and low mechanical properties that restrict its application in gas separation (Achalpurkar et al, 2007; Sheth, 2004). On the other hand, polyurethanes and polyimides are promising materials that have good mechanical properties and better gas selectivities (Huang and Lai, 1995; Yoshino et al, 2000; Yang et al, 2002). In our previous

work, we have reported that the PDMS based polyurethanes show better gas separation process (Madhavan and Reddy, 2006). However, it was observed that increase in PDMS content was associated with a decrease in the mechanical properties and gas selectivities. In order to retain both selectivity and permeability with good thermal and mechanical properties, we have incorporated POSS nanoparticles in the hybrid membranes by chemically reacting functional groups of POSS molecules with the polymer matrices. Here, we have tried to optimize the adopted synthetic strategy to obtain hybrid materials suitable for membrane preparation and expect to have better separation factor for gas mixtures.

1.4.3 Effect of PDMS on thermal properties of PU:

There are many accepted approaches for the improvement of thermal stability of PUs. One of the important approaches is the chemical modification of its structure by blending or copolymerizing with more thermally stable polymers such as PDMS (Wang et al, 2000) or polyimide (PI) (Yeganeh and Shamekhi, 2004). However, the incorporation of PDMS leads to a decrease in the mechanical properties, whereas PI imparts poor solubility. Also, the difficulty in processing techniques limits the usage of PI and PDMS in PUs. The other way of solving this problem is to modify the thermal and mechanical properties of PU by blending nanoparticles into the thin films of diblock copolymers of PU using ZnO nanoparticle. However, the nanoparticles having controlled and well-defined surfaces are needed to control the properties of block copolymers (Zheng et al, 2005). We have developed a synthetic strategy to link up POSS based nanoparticles covalently rather than blending or doping. This methodology stops leaching out of the nanoparticles from the membrane and provides longer life for the usage of membranes.

A very few research works were reported on PU's incorporated POSS macromer because functionalization of POSS macromer to form PU nanocomposite is difficult. Neumann et al (2002) synthesized PU network using isocyanate-functionalized POSS cage and polyethylene glycol. Liu and Zheng (2005) and Liu et al (2006) used amine- and hydroxylfunctionalized POSS cages for the synthesis of PU-POSS nanocomposite. Fu et al. (2001) synthesized POSS group pendant to PU chain. Recently, Oaten and Choudhury (2005) synthesized a POSS-urethane hybrid using isobutyltrisilanol POSS with hexamethylene diisocyanate (HMDI) and they have shown that the POSS incorporation improves the thermal and mechanical stability of thin PU hybrid films. Liu et al (2005) obtained polyurethane networks with POSS by reacting octa(amino)phenylsilsesquioxane with isocyanate terminated polyurethane prepolymer. Thermal stability of hybrid polyurethanes is more than conventional PU elastomer due to nanoscale reinforcement effect of POSS on polyurethane networks.

2. Synthesis of macromers and polymers

The experimental details about the synthesis of allyl-4-nitrobenzoate, synthesis of allyl 4aminobenzoate and the synthesis of POSS-amine were reported by us earlier (Madhavan and B. S. R. Reddy, 2009).

Synthesis of octakis(hydridodimethylsiloxy)octasilsesquioxane (Completely condenced-POSS) (POSS-H) and the synthesis of heptacyclopentyl tricycloheptasiloxane triol (Incompletely condenced-POSS) (CyPOSS) were reported elsewhere (Madhavan et al, 2009). The experimental details about the synthesis of N-(POSS)-7-oxanorbornene-5, 6-dicarboximide (NPONDI) were reported by us earlier (Gnanasekaran and B. S. R. Reddy, 2010).

2.1 POSS-PDMS and POSS-PPG membrane preparation

Into a 100 ml three necked flask, methylene diphenyl diisocyanate (MDI) dissolved in 10 ml of dry THF was added under nitrogen atmosphere. To this, pre-determined amount of PDMS and/or polypropylene glycol (PPG) (M_n =3,500) and POSS-amine (Table 1) dissolved in 20 ml of THF was added at 60°C. Then 1-2 drops of DBTDL catalyst was added and stirred the reaction mixture vigorously for 6 h (Sheme 2). Finally, the reaction mixture was poured into teflon coated glass plate and kept for curing at room temperature. To prevent dust pollution, the glass plate was covered with a filter paper. The hybrid film was then peeled out from the glass plate and dried at 80°C in the atmospheric air for 48 h.

A schematic representation of the membrane formation was given in the schemes 1 and 2.



Scheme 1. Synthesis of POSS-amine


Scheme 2. Synthesis of POSS-PDMS and POSS-PPG hybrid nanocomposites

2.2 Synthesis of PU-POSS hybrid nanocomposites

Into a 100ml three neck flask, hexamethylene diisocyanate (HMDI) was dissolved in 10 ml of dry toluene under nitrogen atmosphere. To this, predetermined amount of PDMS, CyPOSS and POSS-H (Table 1) dissolved in 20ml of toluene was added at 60°C. Then 1-2 drops of dibutyltin dilaurate (DBTDL) catalyst was added and the reaction mixture was stirred vigorously for 6h. The rest of the procedure was adopted as given under POSS-PDMS and POSS-PPG membrane preparation.

A schematic representation of the membrane formation was given in the schemes 3 and 4.

S.No	Sample	PDMS (wt%)	HMDI (wt%)	CyPOSS (wt%)	POSS-H (wt%)	MDI	PPG	POSS- amine
1	PU-POSS-1	70	20	10	-	-	-	-
2	PU-POSS-2	70	17.5	10	2.5	-	-	-
3	PU-POSS-3	70	15	10	5	-	-	-
4	PU-POSS-4	70	12.5	10	7.5	-	-	
5	POSS-PDMS-5	75	-	-	-	20	-	5
6	POSS-PDMS-15	65	-	-	-	20	-	15
7	POSS-PDMS-25	55	-	-	-	20	-	25
8	POSS-PPG-5	37.5	-	-	-	20	37.5	5
9	POSS-PPG-15	32.5	-	-	-	20	32.5	15
10	POSS-PPG-25	27.5	-	-	-	20	27.5	25

Table 1. Various chemical compositions of PU-POSS, POSS-PDMS and POSS-PPG hybrid nanocomposites.



Scheme 3. Model reaction of the monomerfunctional groups



Scheme 4. Chemical structure of PU-POSS hybrids

2.3 Synthesis of homo- and copolymers TFONDI and POSS-ONDI

Ruthenium catalyst 1mg (0.0011mmol) dissolved in CHCl₃ was added to the solution of various compositions of TFONDI and POSS-ONDI macromonomer in chloroform (Table 2). The polymers were precipitated into 100 mL of methanol (yield 80%).

	TFONDI	POSS- ONDI	Mn X 104	PDI	DSC	TGA	
Sample	(wt %)	(wt %)	(g/mol)		Tg (°C)	T ₅ * (°C)	T ₅₀ * (°C)
Homopoly (TFONDI)	100	-	26.65	3.5	175	356	413
POSS25-ONDI	75	25	20.37	1.7	180	336	409
POSS50-ONDI	50	50	5.02	1.4	176	318	398
POSS75-ONDI	25	75	4.28	1.3	173	320	385

 T_5 and T_{50} represents the decomposition temperatures at 5 and 50-% weight loss

Table 2. Molecular weight, feed composition and thermal properties of homopoly(TFONDI) and copoly(POSS-ONDI-TFONDI) nanocomposites

3. Results and discussion

3.1 Synthesis and characterization of POSS-amine macromer

In order to synthesize POSS incorporated hybrid materials, the functionalisation of POSS molecule is essential. To incorporate the functional group into the POSS molecule, hydrosilylation reaction is the best method to introduce the functional group with POSS molecule. Allyl-4-aminobenzoate was introduced into POSS ($Q_8M_8^H$) molecule (Scheme 1) through hydrosilylation reaction using Pt(dvs) catalyst in toluene medium. The macromer synthesized was confirmed well with FT-IR and ¹H NMR. The characteristic Si-H band at 2100cm⁻¹ and the chemical shift at 4.7ppm which was fully disappeared confirming complete substitution in the POSS molecule. The POSS functionalised macromer was further characterized using ²⁹Si NMR spectroscopic technique. Figure 6 shows two chemical shift values corresponding to the two types of silicon atoms present in the macromer. The chemical shift at 13.6ppm corresponds to the silicon atom present at the outer core bonded to the POSS cube and a shift at -108.52ppm was due to the silicon atom present in the core. The presence of these two chemical shifts confirm the complete substitution in the POSS molecule, which further supports that the cube structure of POSS has remained unaltered during the hydrosilylation reaction.



Fig. 6. 29Si NMR of POSS-amine

3.2 Synthesis of POSS-PDMS and POSS-PPG hybrid membranes

Several compositions of POSS-amine incorporated membranes were synthesized and their chemical compositions were shown in Table 1. The POSS incorporated hybrids were characterized using ²⁹Si CP-MAS solid state NMR spectroscopic technique. ²⁹Si-NMR spectrum of the POSS-PDMS-25 hybrid membrane was shown in Fig.7. The spectrum shows three chemical shift values corresponding to three types of silicon atoms present in the membrane. The chemical shift at 14.6 ppm corresponds to the silicon atom (b) present in the outer core bonded to the POSS cube. The shift at -110.23 ppm was due to the silicon

atom (a) present in the inner core. The chemical shift at -25 ppm was due to the silicon atom (c) of linear siloxane chain of membrane matrix. These chemical shifts were very close to the reported values by Sellinger et al (2007). The presence of chemical shifts at 14.6 ppm and - 110.23 ppm confirms the cubic structure of the POSS molecule which was unaltered during the formation of hybrid membrane.



Fig. 7. ²⁹Si CP-MAS solid state NMR spectroscopic of POSS-PDMS and POSS-PPG membrane hybrids

3.3 Synthesis of homo- and co-polymers of TFONDI and POSS-ONDI

Phenyl-capped silsesquioxane POSS-Ph, POSS-Ph-NO₂, POSS-Ph-NH₂ and N-(POSS)-7-oxanorbornene-5,6-dicarboximide were reported by us earlier (Gnanasekaran and B. S. R. Reddy, 2010).

The homopolymer of TFONDI and the copolymers of TFONDI and POSS-ONDI have been prepared using the Grubbs ring opening metathesis polymerization (ROMP) catalyst. Attempts to prepare the homopolymer of POSS-ONDI was not successful, presumably due to the steric hindrance imposed by the bulky POSS group. The ¹H NMR spectra of the homopolymer of TFONI and of copolymers exhibited the expected shifts at 6.0 (trans), 5.8 (cis), 5.1 (cis), 4.6 (trans) and 3.4 ppm.

3.4 Synthesis and characterization of PU-POSS hybrid nanocomposites

In this work, we have tried to incorporate both completely condensed POSS and incompletely condensed CyPOSS into the PU matrices. Hence, we have chosen the incompletely condensed CyPOSS molecule with a hydroxyl functional group to form urethane linkage with the isocyanate group. On the other hand, the completely condensed POSS-H molecule with hydride functional group, having an ability to react with the hydroxyl functional group of incompletely condensed CyPOSS molecule in the presence DBTDL catalyst (Schemes 3 and 4). The hybrid films synthesized were characterized using FTIR. FTIR technique was found to be quick and accurate method to determine the chemical



Scheme 5. Synthesis of macromonomer, homopoly(TFONDI) and copolymers of POSS-ONDI and TFONDI

structure of PU hybrids. The characteristic band near 2270 cm-1 represents the isocyanate group. This was completely disappeared in the IR spectrum of all the PU-POSS hybrid films, confirming that all the isocyanate molecules were completely reacted with the hydroxyl groups of CyPOSS and PDMS chain. On the other hand, the Si-H of POSS band near 2100cm-¹ was also completely disappeared for all the PU-POSS films. We have anticipated that the Si-H condensation reaction with Si-OH in the presence of DBTDL catalyst may not proceed completely due to bulkiness of the POSS molecule. But in this case, surprisingly all the POSS was completely reacted and forming CyPOSS-POSS linkage and showing the complete distribution of POSS in the PU-POSS nanocomposites. The band near 1627cm⁻¹ shows the formation of (C=O) urethane linkage with Si-OH group and 1590cm⁻¹ showing the formation of (C=O) urethane linkage by CH₂-OH. A very broad band near 3341cm⁻¹ corresponds to the hydrogen bonded N-H urethane linkage, which confirms the existence of hydrogen bond formation between the urethane linkages. PU-POSS hybrids show two bands at 1104 and 1013cm-1 corresponding to the Si-O-Si linkage of the POSS cubic structure and Si-O-Si linkage of the PDMS straight chain. The band at 1104cm⁻¹ (Si-O-Si cube) was observed in all the PU-POSS films suggesting that the POSS cube has remained intact during the nanocomposite formation.

3.5 Thermogravimetric analysis of POSS-PDMS/PPG hybrid membranes 3.5.1 Complete-POSS

The thermal stability and degradation behaviour of PU-POSS hybrids were examined using TGA. The TGA was performed in the N₂ atmosphere and the TGA values of PU-POSS hybrids were shown in Table 3. The POSS based hybrids show enhanced thermal properties like initial decomposition temperature (IDT) and the char yield values when compared with POSS free PU hybrids. The initial decomposition near 270°C is mainly attributed to the degradation of labile urethane group present in the hybrids. It was observed that the incorporation of increased wt % of POSS molecules increases the IDT of the hybrids. The char yield values for the POSS incorporated hybrids show higher value (20-30 wt% at 600°C), indicating the rigid POSS cubes which remain stable even at higher temperatures. This indicates that the degradation of labile urethane group was controlled by the POSS rigid molecules. All the PPG soft segment based hybrids show decomposition pattern similar to the PDMS based hybrids. For all the hybrids, increase in the crosslinker (POSS) content increases the thermal properites of the hybrids. That means the IDT and char yield values increases with increase in the POSS content. This proves that POSS macromers improve the thermal properties of the hybrids to a greater extent. Zheng et al (2006) reported that the increase in POSS content does not alter the degradation pattern of the PU hybrids. But, the char yield values and T_{max} varies with POSS content. The literature reported incorporation of POSS molecule enhances the thermal properties of the hybrids (Moreau et al, 2004). Based on the TGA results, it was possible to suggest that POSS nano cubes based hybrids possess enhanced thermal properties of hybrids.

3.5.2 Incomplete-POSS

The thermal stabilities of the PU-POSS hybrids were characterized with TGA under N_2 atmosphere and the TGA data of PU-POSS hybrids were shown in Table 3. The initial decomposition for all the PU-POSS were similar and the initial decomposition (5 wt%) starts at 268°C for all the PU-POSS hybrids showing with excellent thermal stability. The decrease in

the thermal properties was observed for PU-POSS hybrid films with increase in the addition of completely condensed POSS group. The CyPOSS substituted hybrid shows a very high thermal stability due to the presence of thermally stable cyclopentyl group in the vertices of CyPOSS group and likely the formation of more hydrogen bonding compared to methyl substitution in the POSS-H group. Incorporation of 2.5 Wt% of completely condensed POSS-H into the PU-POSS matrices show very high decrease in thermal properties of the PU-POSS-2 hybrid film. On further increase in the POSS-H incorporation, thermal properties slightly increased for the hybrids as observed in PU-POSS-3 and PU-POSS-4. But, the improved thermal properties of these hybrids were quite low compared to PU-POSS-1 hybrid film. The completely condensed POSS and incompletely condensed POSS incorporated PU-POSS hybrids (PU-POSS-2, PU-POSS-3 and PU-POSS-4) show two stage decomposition and the incompletely condensed POSS incorporated hybrid (PU-POSS-1) shows a single stage decomposition. These observations indicate that the completely condensed POSS molecule relatively affects the thermal properties of PU-POSS hybrids even at lower concentration. The final residue for PU-POSS-1 and PU-POSS-2 hybrids at 700°C remains the same, where as the residue increases in the case of PU-POSS-3 and PU-POSS-4 hybrids with increase in the concentration of completely condensed POSS. This clearly shows that the POSS-H aggregates remain unaltered even at 700°C but the contribution of completely condensed POSS-H for the polymer matrices as a whole towards thermal properties appears to be very less. From these observations, it was concluded that the nature of the POSS group, reactive functional group in the POSS molecule and the rigid bulky group on the vertices of the POSS were the three main factors which significantly alter the thermal properties of the hybrids.

3.5.3 Copolymers of POSS-ONDI and TFONDI

The decomposition temperature and the char yield values of the polymers were listed in Table 2. It was observed that the incorporation of POSS (e.g., copolymers of POSS-ONDI) decreased the thermal stability of the polymers, whereas TFONDI homopolymer showed very high thermal stability. The addition of POSS decreased the thermal stability of POSS-ONDI copolymers due to the disruption of close packing of the polymer units by the bulky POSS groups and leads to an increase in the free volume between the polymer chains. The overall observation suggests that the POSS molecule affects the thermal properties of polymers of N-(POSS)-7-oxanorbornene-5,6- dicarboximide nanocomposites even at low concentrations.

3.6 Differential scanning calorimetric analysis.

The DSC values of POSS incorporated hybrid membranes were shown in Table 3. The POSS/PPG incorporated hybrids show two distinct glass transition temperatures (Tg's). The lower Tg values around -48 to -40°C was attributed to the PPG soft segment and the Tg around 179 - 185°C was due to the PU hard segment (Reddy et al 2009). The Tg values of POSS incorporated hybrids were given in Table 3. The Tgs corresponding to the hard segment increases drastically with increase in the POSS incorporated hybrid membranes. This indicates that the POSS rigid cube restricts the free rotation of the macromolecular chains to a greater extent.

The nanocomposite membranes showed an enhanced *Tg*, with increase in the POSS content. The *T*gs at 197, 191, and 220°C were observed for 5, 15, and 25 wt% of POSS incorporated membranes, respectively. The increase in *Tg* for POSS incorporated membranes was due to

SAMPLE	T ₅ (°C)	T ₅₀ (°C)	Char yield at 600°C (%)	$Tg_{(Hs)}$ (°C)
PU-POSS-1	268	465	10	195
PU-POSS-2	268	413	8	197
PU-POSS-3	269	404	15	191
PU-POSS-4	270	388	10	220
POSS-PDMS-5	225	380	22	179
POSS-PDMS-15	250	382	25	185
POSS-PDMS-25	260	390	28	189
POSS-PPG-5	270	380	17	180
POSS-PPG-15	273	365	20	183
POSS-PPG-25	275	385	26	185

Table 3. TGA and DSC Values for PU-POSS, POSS-PDMS and POSS-PPG based PU hybrid nanocomposites

the nano-reinforcement of POSS molecule in the polymer matrices, which restricts the motions of polymer chains (Madhavan and Reddy, 2009). Tgs at 197, 191, and 220°C were observed for PU-POSS-2, PU-POSS-3 and PU-POSS-4 nanocomposite membranes, respectively.

The glass transition temperature of the POSS-ONDI nanocomposites was significantly enhanced by the incorporation of 25-wt % of POSS units. This may be due to the restricted motion of the polymer chains caused by the even distribution of bulky POSS units at the segmental level and increased rotational barrier of the polymers at low POSS concentration. But, the Tg values were lowered when the loading of POSS units increased to 50 or 75-wt %. This effect could be possibly explained by the fact that the bulky POSS creates more chain spacing resulting in the increase in free volume with larger fraction of low molecular weight component giving raise to the decrease in the Tg values.

3.7 Dynamic mechanical analysis

3.7.1 Complete-POSS

The storage modulus values (E') of PU hybrids were shown in Table 4. It was observed that E' was increased by incorporating a small amount of POSS into the hybrid. E' values for all the POSS hybrids were higher than those of linear PDMS chain incorporated hybrids. The E' values at 30°C were found to be 9.1, 14.6, 18.2, 29.2, 32.1 and 35.0 for POSS-PDMS-5, POSS-PDMS-15, POSS-PDMS-25, POSS-PPG-5, POSS-PPG-15 and POSS-PDMS-25 respectively. The increasing % of POSS incorporated hybrids show three fold greater than that of the free POSS content hybrids. This implies that the incorporation of the POSS nanoparticles play an important role in the viscoelastic behaviour of the synthesized hybrids. The hybrids show a very long range of rubber plateau region since all the hybrids contains almost 90% of both the PPG and PDMS soft segments. The enormous increase in the storage modulus of the nanohybrids even at low concentration of 15wt% of POSS (POSS-PDMS-15) incorporation confirms that the contribution of POSS cage structure towards the increase in viscoelastic properties of the nanohybrids. The Tg values significantly increased with the increase in the incorporation of the POSS content as explained in the DSC analysis. The Tg values obtained through DSC measurements were found to be in good agreement with the Tg values obtained from the DMA measurements. For the POSS incorporated PU hybrids, the tan δ values were found to be very high and the peaks were broadened, when compared to the PDMS incorporated PU hybrids. The high δ peaks show even distribution of POSS molecules in the PU network structure.

Sample	Storage Modulus (E') at 30ºC	Tg (PDMS soft segment)	Tg (PPG soft segment)	Tg (HS)
POSS-PDMS-5	9.1	-112	-	162
POSS-PDMS-15	14.6	-104	-	164
POSS-PDMS-25	18.2	-101	-	169
POSS-PPG-5	29.2	-105	-33	168
POSS-PPG-15	32.1	-107	-29	170
POSS-PPG-25	35.0	-108	-23	175

Table 4. DMA results of POSS-PDMS and POSS-PPG based PU hybrid nanocomposites

3.7.2 Incomplete-POSS

The bending storage modulus (E') versus temperature curves at 0.1 Hz for PU-POSS hybrids were shown in Figure 8. The decrease in E' with increase in the concentration of completely condensed silsesquioxane was observed. E' value of PU-POSS-1 was higher than that of the mixed CyPOSS and POSS hybrid films such as PU-POSS-2, PU-POSS-3, and PU-POSS-4. This is due to the CyPOSS-urethane interaction with polymer matrix and the formation of hydrogen bonding in the case of PU-POSS-1. The decrease in the storage modulus of PU-POSS-2, PU-POSS-3 and PU-POSS-4 perhaps attributed to the formation of hydrophobic



Fig. 8. The storage modulus (E') Versus Temperature curves of PU-POSS hybrid nanocomposites

CyPOSS-POSS aggregates in the matrices. This in turn reduces the interchain interactions and interrupts the PU hydrogen bonding formation. All these factors suggest that the contribution of POSS cage structure alone may not be enough to improve the mechanical properties. However, the cage interaction with the polymer matrix and their functional groups were all highly dependent on each other.

3.8 Atomic Force Microscopy (AFM)

Surface morphology of PU-POSS nanocomposite membranes was examined by AFM. The images of PU-POSS-2 and PU-POSS-4 were shown in Figures 9 and 10. It was observed clearly that the spherical domains correspond to POSS clusters which spread over the surface of the membranes. This may be most likely due to the incompatible nature of POSS molecule with polymer matrices and confirms that even the crosslinking of POSS with polymer matrices through functional group will not restrict the formation of aggregation of a POSS nanoparticle (Madhavan and Reddy, 2009). In the case of nanocomposite



Fig. 9. AFM images of PU-POSS-1



Fig. 10. AFM images of PU-POSS-2

membranes with POSS nanoparticles show more granular type POSS aggregates with rough membrane surface area indicating that the surface morphology of membranes was highly affected by the addition of POSS molecule to PU-POSS membranes. The AFM image reveals a highly heterogeneous morphology reflecting the less dispersive nature of POSS molecules with PDMS-PU hybrids.

The AFM image of TFONDI was slightly different from the POSS incorporated nanocomposites, showing a smooth surface having microphase separated morphology. It was observed that a uniform distribution of spherical POSS aggregates dispersed in the nanocomposites. In the case of our systems, the aggregation of POSS might be created by self-assembling of POSS.

3.9 Transmission Electron Microscopy (TEM)

TEM imaging analysis of the polymers (Fig.11) provide further information about the POSS dispersion in the polymer matrix. No particles could be observed for the transparent TFONDI. However, transmission electron microscopy of POSS25-ONDI revealed nano-sized POSS clusters with varying sizes ranging from 50 nm examined in various areas of the film surface. TEM imaging POSS domains were darker than the polymer matrix because of their higher mass contrast in comparison with polynorborene-imide chains. This observation also showed that the discreetly sized POSS cage aggregates were well dispersed within the bulk polymer (Zeng and Zheng, 2007).



Fig. 11. TEM images of homopolymer of TFONDI (right) and copolymer of POSS25-ONDI (left).

3.10 Scanning Electron Microscopy (SEM) analysis

Figure 12 display SEM images of the bulk morphology of PU-POSS-1, PU-POSS-2, PU-POSS-3 and PU-POSS-4 hybrid films. All the PU-POSS films show a microphase separation of urethane hard segments and a micro/nano level spheroidical aggregation of POSS rich domains. Similar observations were reported (Zhang et al, 2006) about the aggregation of POSS from nano- to micro- level, and the hydrogen bonding increases the compatibility in the phenolic reisn-POSS hybrid nanocomposites. It can be clearly seen in the SEM images that the POSS aggregates in to POSS rich spheroidical domains in the PU-POSS hybrid films. But the type of aggregation of POSS groups and the phase separation in the all films were



PU-POSS-3

PU-POSS-4

Fig. 12. SEM images of PU-POSS nanocomposites

found to be different. There was an excellent dispersion of CyPOSS-urethane aggregates in the PU-POSS-1 film. The aggregations were not homogeneous in the case of PU-POSS-2, PU-POSS-3 and PU-POSS-4 films and were highly phase separated from the polymer matrix. The excellent dispersion of CyPOSS-urethane aggregates in the PU-POSS-1 was explained by the combination of three factors. i) The reactivity of trisilanol group with isocyanate so that it can incorporate CyPOSS evenly in the network during the early stages of the polymerization. ii) The high compatibility of CyPOSS in the PU matrices rather than completely condensed POSS-H, where the CyPOSS interacts highly with the polymer matrices. iii) The possibility of favourable CyPOSS- CyPOSS organisation in the PU matrices. The combination of these three factors create a homogeneous aggregation of CyPOSS-urethane and even distribution of aggregates in the polymer matrices (Madhavan et al, 2009). The PU-POSS-2, PU-POSS-3 and PU-POSS-4 hybrids show a large fraction of POSS aggregation and inhomogeneous aggregations. This may be due to the formation of hydrophobic CyPOSS-POSS aggregates, which seems to be having less interaction with polymer matrices. The fraction of POSS aggregation increases with increasing in the addition of completely condensed POSS-H cage structure.

3.11 Wide-Angle X-ray Diffraction (WAXD)

1) The microstructure of PU-POSS hybrids was of further interest to us and studied using the WAXD measurements. Fig. 13. displays XRD patterns of PU-POSS hybrids. For comparison, the diffraction patterns of pure CyPOSS and POSS-H were also shown. The pure Cy-POSS and POSS-H molecules show crystalline peaks at 2θ = 7.0°, 10.2°, 11.5°, and 18.3°. All the crystalline peaks of Cy-POSS and POSS-H peaks were absent in the PU-POSS hybrid films. This implies that the crystallinity of POSS molecules were collapsed by the polymer matrices in the PU-POSS hybrids. A broad peak at 2θ =11.3° in all the hybrids was observed, which may be due to the amorphous nature of the PDMS matrices. These observations could reflect that the absence of crystalline microdomains in the POSS rich phase and also confirms the absence of macrolevel POSS aggregation in the PU-POSS hybrids.

2) The WAXD pattern of POSS-PDMS-25 and POSS-PPG-25 hybrid membranes were measured and the results were shown in Fig. 14. A broad diffraction intensity was observed around $2\theta = 11.0-13.5^{\circ}$ which may be due to amorphous PDMS soft segment present in the matrices. It could be seen that a very weak peak *ca* at $2\theta = 18.3-21.0^{\circ}$ in the hybrids reflect the amorphous PU groups present in the membrane matrix. After hybridization, the crystalline peaks of bulky POSS groups were absent in the membrane matrices showing that the membranes were found to be highly amorphous in nature. Similar observations were reported by Chang et al, 2004.



Fig. 13. WAXD curves of Pure-POSS-H, Pure-CyPOSS and PU-POSS hybrid nanocomposites



Fig. 14. WAXD curves of POSS-PPG-25 and POSS-PDMS-25 hybrid nanocomposites

3.12 Pressure dependency of permeability of membranes

Solution-diffusion transport model was applied for gas transport process through dense polymer film. The permeability coefficient (P_A) of a penetrant through a membrane was measured as a steady state flux (N_A), normalized by partial pressure difference (ΔP_A) and membrane thickness (d).

$$P_A = N_A \frac{d}{\Delta P_A}$$

Permeability is frequently expressed in Barrers, where 1 Barrer= 10^{-10} cm³ (STP) cm/cm² s cmHg. Permeability coefficient of a particular penetrant can also be expressed as the product of a kinetic factor, the diffusion coefficient (D_A), and a thermodynamic factor, the sorption or solubility coefficient (S_A).

$$P_A = D_A S_A$$

Membrane separation performance is characterized by ideal selectivity of a membrane, $\alpha_{A/B}$ when the downstream pressure is negligible. This ideal selectivity is defined as the ratio of permeabilities of two gases and is the product of diffusivity selectivity D_A/D_B and solubility selectivity S_A/S_B , of two gases in the membranes.

$$\infty_{A/B} = \frac{P_A}{P_B} = \left(\frac{D_A}{D_B}\right) \left(\frac{S_A}{S_B}\right)$$

Permeability of N_2 and O_2 gases drastically decreases with the increase in penetrant pressure for all the POSS incorporated membranes. This may be due to two factors. (i) When

the penetrant pressure increases, there must be a compression of polymer matrix which leads to reduction in the free volume for penetrant transport. This in turn reduce penetrant gas diffusion coefficient. (ii) The other factor may be due to the dispersion of POSS aggregates on the surface of membranes, which restricts the interaction of penetrant with the surface of the membrane matrices. If the penetrant's pressure increases, adsorption of lighter gases on the surface of membrane may likely decreases due to the POSS aggregates. This leads to a decrease in permeability of gases. In the case of CO₂, the permeability was found to be quite different and increases with the increase in pressure. This perhaps may be due to more condensable nature of CO₂ gas. Also, by increase in pressure, the adsorption of CO₂ gas on the surface of membranes seems to be high and the diffusion of CO₂ gas was more when compared to that of N2 and O2 gases. But, it was observed that at higher POSS content the increasing order of CO₂ permeability was slightly reduced with pressure, due to the restriction of interaction of CO_2 with membrane matrix by the presence of POSS aggregates. Incorporation of nonporous (impermeable) nanoparticles to polymer membranes unfortunately tends to reduce penetrant's permeability. This effect can be accurately modelled by Maxwell's relationship (Maxwell 1873) originally derived to describe the dielectric properties of suspension of spheres and this can also be used to model permeability of membranes filled with spherical impermeable particles. In this work, we have observed that the CyPOSS content in all the compositions decreases permeability drastically in N₂, O₂, and O₂ gases (Maxwell relationship). This indicates that increase in the CyPOSS nanoparticle volume fraction tends to reduce the permeability. But, many researchers reported that the incorporation of inorganic nanoparticles like fumed silica in polymeric membrane leads to increase in permeability of gases, showing non-Maxwellian's effect (Moaddeb and Koros, 1997; Patel, 2003). Cong et al, 2007 explained the non-Maxwellian's effect of nanocomposite membranes was due to poor compatibility between silica surface and the polymer chains. This could not organise the nanoparticles to have tight packing, whereby forming a narrow gap surrounding the nanoparticles. The gas diffusion path was shortened and thus apparent gas diffusivity and permeability were increased. On the other hand, non-Maxwellian's effect was described using a slightly different phenomenon where silica nanoparticles were small enough to disrupt polymer chain packing in the polymers. This resulted in an increase in polymer fractional free volume which increases the permeability of the membranes. Similar observations were made by Gonzalez et al, (2006) who reported an increase in POSS concentration increases the permeability of all gases due to nanocracks or nanogap formation in the membranes. But, modified silica nanoparticle (Cong et al, 2007) incorporated membranes show decrease in permeability of gases. Similar decrease in the permeability with increase in POSS concentration was observed in the case of CyPOSS incorporated nanocomposite membranes. Lin and Freeman reported a drastic decrease in permeability in the case of poly(trimethylsilylpropyne) membrane containing POSS nanoparticles. The CyPOSS nanoparticle incorporated PDMS-PU membranes show decrease in permeation with increase in POSS concentration for all gases (Maxwell's effect). But, surprisingly there was slight increase in the permeability when the POSS-H content was added to CyPOSS incorporated membranes (non-Maxwell's effect). This may be due to the poor compatibility of POSS-H aggregates forming heterogeneous dispersion over the membranes. This causes the disruption of polymer chain packing and resulted an increase in the free volume. The

increase in free volume was well corroborated with the decrease in the measurement of density of the membranes. Based on the above observations, it was predicted that the compatibility of POSS nanoparticles alter the permeation of diffusing molecules. POSS molecule either aids the formation of more free volume or provides torturous route for penetrant diffusion depending upon the compatibility. In the case of CyPOSS incorporated nanocomposite membranes, the dispersed POSS phases act as a blocking agent and produce higher resistance route for diffusing molecules.

3.13 Selectivity of the membranes

Selectivity of O_2/N_2 gas pair was in the range of 1.9–2.4 and for CO_2/N_2 was 7.4–14.9. Figs. 15 and 16 represent O_2/N_2 and CO_2/N_2 gas pair selectivities of membranes as a function of pressure. The O_2/N_2 gas pair selectivities increased slightly with the increase in POSS content as well as with pressure. This seems to be mainly due to high interactions between O_2 gas and high concentration of silicon and oxygen atoms that constitute POSS cage. It is reported that O_2 gas has more interaction with the polar groups and silicon atoms of polymers that lead to higher solubility of oxygen gas in the membranes (Khotimskii et al, 2000). In the case of CyPOSS incorporated membranes, an increase in the POSS content leads to the presence of either more urethane linkages or unreacted triol functional groups of POSS and Si atoms of POSS molecules in the membranes. But, the addition of POSS-H to



Fig. 15. O2/N2 gas pair selectivity as a function of pressure.



Fig. 16. CO_2/N_2 gas pair selectivity as a function of pressure.

nanocomposite membranes does not increase the O_2/N_2 selectivity. This might be due to the restriction in the formation of urethane linkages by the POSS-H molecule as we have reported earlier (Madhavan et al 2009). Likewise, the selectivities of CO_2/N_2 gas pair increases from 7.4 to 14.9 with an increase in POSS content and pressure, whereas CO_2/N_2 selectivity was slightly decreased by the addition of POSS-H nanoparticles. This shows that selectivity parameter was controlled by the diffusion of gas molecule through the urethane polar groups rather than the POSS aggregates in the membrane.

4. Conclusions

A new class of ester, aliphatic, aromatic-amine functionalised silsesquioxane macromers, completely condensed and incompletely condensed POSS were synthesised and these macromers were used to synthesize poly(ester-urethane), polyimide and polyurethane-POSS nanocomposites. Linear poly(dimethylsiloxane) was also synthesized to study the influence of different wt% of silsesquioxane macromer, PDMS macromer and a series of PU-POSS hybrids consisting of various compositions of completely condensed and incompletely condensed POSS hybrids were synthesized. Thermal, mechanical, morphological and surface properties of POSS based hybrids were studied using TGA, DSC, SEM, TEM and

AFM. Based on the char yield values of the hybrids, it was observed that a slight increase in the thermal properties of the silsesquioxane incorporated PU networks than that of the linear PDMS macromer incorporated hybrids. The TGA thermograms of the macromers reveal that the thermal stability depends on both the functional group substituted and the structure on the siloxane compound. The DSC values of macromers show that the thermal transitions were mainly dependent on the functional group substituted in the inorganic core. The glass transition temperatures of the POSS incorporated PU networks increases with increase in the wt% of POSS. This may be due to the increasing number of bulky POSS which makes the membrane to vibrate the polymer chain giving rise to higher Tgs. The surface morphology was highly affected by the POSS molecule and this may be due to formation of nano/micro level spheroidical aggregations. The mechanical and thermal properties were enhanced by the formation of these aggregates since these aggregates act like spacers between the polymer chains due to its incompatible nature with the PU-POSS matrices. TEM and AFM micrographs of nanocomposites were consistent with a selfassembled spherical aggregation of POSS dispersed in POSS based nanocomposites. The absence of crystalline domains due to POSS molecule in the membranes were found to be highly suitable for gas separation process since the crystalline domains in the membrane affect the permeability of gases. Permeability measurement reveals that the permeability of N2 and O2 gases decreases with the increase in pressure. The permeability of all the gases decreases with the increase in the incomplete condenced-POSS nanoparticle concentration. But, addition of a small concentration of complete condenced-POSS nanoparticles to incomplete condenced-POSS based membrane increases permeability while selectivity of O_2/N_2 gas pair decreases. This reveals that the nature and compatible of POSS groups alter the permeability of gases and the polar urethane linkages play a vital role in the gas pair selectivities of nanocomposite membranes. The selectivity of O2/N2 gas pair was in the range of 1.9-2.4 and for CO_2/N_2 pair from 7.4 to 14.9. The overall conclusion drawn from all the observations was that the rigid POSS cubic cage structure alone was not imparting the properties to the bulk polymer, but the functional group, compatibility of the POSS molecule with the polymer matrices and bulky substituents in the vertices of the POSS molecules alters the bulk properties of the polymers.

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Rheology-Morphology Interrelationships for Nanocomposites based on Polymer Matrices

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1. Introduction

Nanocomposites based on polymer matrices are heterogeneous systems containing nanodispersed fillers distributed in polymer. The main aim of developing this kind of materials is to reinforce commodity thermoplastics giving them some functional properties (low flammability, increased barrier behavior, higher heat deflection temperature, and so on). When fillers are nanoscopic, there are advantages afforded to filled polymers and composites that lead to performance enhancements. These advantages results primarily from filler size reduction and the concomitant increase in interface. This means, that development of materials with unique or improved properties does not demand creation of new chemical manufactures for production of new and, as a rule, expensive polymers. For this reason the high activity of various research groups in the field of detail investigation of structure and properties of nanoparticles of different nature and composite materials on their base is being observed.

The main portion of this activity is devoted to search and detail characterization of nanoparticles of various nature (nanoclays, nanodiamonds, metals and their oxides, salts and specific compounds, for example CdSe, playing the role of quantum dots, and others). Remaining fillers for specific functional application outside the scope of this Chapter, we intend to consider here very simple nanofillers, such as clays and nanodiamonds serving for the development of a new family of engineering plastics. At literature analysis it is possible to understand that a lot of has been devoted to the attention elaboration of preparation methods, their characterization by different methods, and mechanical properties of final products (see, for example, Pinnovaia & Beall, 2000). Meanwhile, approaches to compatibility of particles and polymer, as well as their processing, remain on "periphery of main stream". We would like to fill this gap by information based on our experience, i.e., to consider some methods of compatibility of particles with polymers, rheological properties of nanocomposites precursors, interrelationships between rheology and morphology for heterophase viscoelastic media and approaches to their processing.

The crucial question appearing at realization of nanocomposite concept consists in: "Why nanofillers reinforce polymer with a high efficacy?" There are different versions of answer

this question. All of them are based on superhigh interfaces in such systems, but the angle of vision is different. In our opinion, the main reinforcing effect comes from polymers due to the absorption of macromolecules onto external (e.g. nanodiamonds) or internal (intercalated layered silicates) surfaces of nanoparticles, realization of their "non-natural" conformations, formation of dense adsorption layers, separation of conformations between volume and adsorbed layers. This proceeds at melt mixing of particles with polymer. Solidification of precursors by cooling (thermoplastics) or crosslinking (reactive resins) leads to "freezing" these conformations for amorphous polymers or to specific crystallization behavior for semi-crystalline polymers. The term "specificity" in this case means that depending on macromolecular conformations in liquid precursor the final crystalline structure of polymer in solid nanocomposite will be changed.

It other words, the introduction of nanodimensional particles modifies the structure of polymer. All these events take place at minor content of nanofillers, less than percolation threshold. At higher concentration only a possibility to form by particles the arming network appears but this is another story.

Based on above mentioned concept, the reinforcing effect should be especially expressed at homogeneous distribution of particles, but all of them due to high interfacial energy and presence on the surface of functional groups (e.g., nanodiamonds of detonation synthesis) inclined to form aggregates. That is why, the task number one is to introduce minor content of particles to polymer as possible homogeneously for distribute them to avoid large aggregates. It would be fine, if disaggregation procedure could be involved to compatibility process. We will consider various methods of compatibility tested by our group on an example of nanodiamonds keeping in mind above written requirements. The task number two consists in detail investigation of rheology-morphology interrelationships that is extremely important for all heterophase systems, because flow may influence significantly on nanoparticles distribution. Since flow is obligatory factor of processing, the distribution of particles reached at mixing could be changed during processing. The task number three relates to rheology-structure interrelationships where the term "structure" concerns crystallographic level as polymer, as nanofiller. The possible correlations between rough morphological and fine structure levels should be estimated. This is very important for final properties of nanocomposites, and among them mechanical characteristics are dominant. All these tasks will be considered in this Chapter.

2. Objects

As a matrix, series of polymers of different polarities have been used: hydrophilic hydroxypropylcellulose (HPC), capable to form liquid crystal (LC) phase as in melt, as in solution, styrene-acrylonitrile copolymer (SAN), polysulfone (PSF), polyisobutylene (PIB), and others.

The majority of experiments were carried out on two kinds of nanofillers: Namontmorillonite (Cloisite Na+) and organoclays (e.g., Cloisite 15A) produced by Southern Clay Products, USA, and nanodiamonds (ND) of detonation synthesis (Shenderova, 2004; Detkov et al.). ND were prepared by "Electrochimpribor", Russia (trade mark "PUOO-SH – 96"), weight fraction of ND in a powder is not less than 98 %, density is 3.3 g/cm3.

In spite of the fact that individual particles of both fillers have nanodimensions, there exist aggregates of micron size in the powder. The main problem here is to find the appropriate method of combining particles with polymer.

Four methods have been tested:

- 1. Traditional mechanical mixing at temperature higher melting or softening points ("standard mixing") (Karbushev et al., 2007);
- Melt mixing at very high shear rates, i.e., in conditions close to elastic turbulence and instability of melt flow as whole (Vinogradov & Malkin, 1966; Malkin, 2006; Karbushev et al., 2008), where turbulent vortexes and probable cavitation zones could induce disaggregation of large particles;
- Deposition of particles on a surface of polymer grains distributed in inert liquid medium at ultrasonic action with subsequent removing inert liquid by filtration and drying nanocomposite precursor (Konstantinov et al., 2009; Karbushev et al., 2009);
- 4. Introducing of particles to polymer solution at sonication with subsequent removing a solvent (so-called "solution method") (Karbushev et al., 2007).

The first method, the most suitable for thermoplastics, was used as the reference method. It was realized on laboratory mixer of screw-plunger type with operating volume of 4-5 ml (Fig.1). Mixing procedure takes 7 min at temperatures 135-150°C (HPC), 200-220°C (SAN) and 280-300°C (PSF). Rotation of screw is around 60-80 rpm and nanocomposite precursor circulates not only in radial, but also in axial directions. Then, plug 6 was avoided, and the filled melt extrudes through a capillary with 1/d=20/1 (mm).



Fig. 1. Scheme of screw-plunger mixer: 1- engine; 2 - screw; 3 - working chamber; 4 - electric furnace; 5 - capillary; 6 - catch gear (plug); 7 - baseplate; 8 - holder.

The second mixing method is also based on a direct combining of particles with polymer melt, but at super-high shear rates, i.e., in a regime of elastic instability. The same apparatus as before has been used but fast rotation of a screw (600-800 rpm) allowed us to reach shear stresses of 10⁵-10⁶ Pa for SAN and 10⁶-10⁷ Pa for PSF. According to classical papers of Vinogradov et al. (Vinogradov et al., 1966; Vinogradov & Ivanova, 1968), at such conditions so-called "spurt" takes place, i.e., abnormal increase of shear rate at approximately constant shear stress. "Spurt" was explained as relaxation transition of melt to rubber-like state induced by shear, loosing of tack to the wall of capillary and slippage. Polymer in a slippage step relaxes to melt state and becomes tacky again, sticking to the wall. Repeating cycles of

"stick-slip" leads to appearance of defects of various topology on the extrudate surface: shark-skin, spirals, waves, and so on.

Subsequent numerous investigations have considered this phenomenon in details under different vision angles, and suggested some new mechanisms and driving forces (Yarin & Graham, 1998; Yang et al. 1998), but for the aim of this Chapter the important feature is irregularity of a stream only. It is a "tool" we tried to use to disaggregate large particles formed by nanoparticles connected by dispersion interactions Van-der-Waals and electrostatic forces.

The "colloidal-deposition" method consisted in disaggregation and dispersion of the filler particles in a low-molecular-weight liquid medium, inert towards the polymeric matrix, subjected to the action of an ultrasonic field. A polymer powder was added to the polymer suspension without terminating the intermittent sonication. Under these conditions, the so-called heteroadagulation occurred, e.g., nanodiamond particles are deposited (immobilized) onto the surface of coarser polymer particles. As the process was complete, the solid phase was separated by filtration, dried, and nanocomposite precursors were processed by extrusion or hot pressing. Because of the lack of analogies, this way to produce nanocomposites was named as "colloidal-deposition" method.

Several composites were obtained by popular laboratory method via polymer solutions. For this purpose, the filler was dispersed in a polymer solution under the action of ultrasound. We used 4% solutions of HPC in distilled water, SAN in acetone, and PSF in chloroform. In this case, composite films were produced by casting, followed by evaporation of the solvent. Thin slices of nanocomposite precursors prepared according above mentioned methods were cut and characterized by optical and electron-microscopical methods. The special program of digital images analysis has been developed in frames of MathLab 7.0. It was very significant step to analyze dimensions of particles directly in polymer matrices, but not in model dispersions. Optical images of nanocomposites containing 1% of ND in SAN matrix are shown in Fig.2.

As is seen, the homogeneity of particles distribution and their dimensions depend essentially on mixing method. The best results were achieved by mixing in "spurt" regime and via stage of colloidal deposition. The distribution curves in optical domain of dimensions are presented in Fig.3.

Maximum of distribution curves for all blends is located in the dimension region of 1-2 mkm, but its sharpness is different. The most narrow maxima are observed for "spurt" regime and method of colloidal deposition. For standard mechanical mixing and solution method more flat maxima and presence of large agglomerates are observed.

For estimation of dispersity degree in sub-micron domain the transmission electron microscopy has been used. Micrographs of specimens with different magnification one can see in Figs 4 and 5. From the qualitative view point samples obtained via "spurt" and "colloidal deposition" methods are much better than the reference sample.

The quantitative analysis has shown that melt mixing in "spurt" regime is the best: the maximum fraction of particles is located around ~40 nm while for colloidal deposition method its position is 80-120 nm. The generalized polydisperisty curve for nanocomposite SAN-1% of ND is presented in Fig.6

All set of data shows that melt mixing in "spurt" regime is the best and looks like very attractive for application, because high-speed mixers can be used and the process does not contain any solvent that should be recuperated and regenerated. An attempt to reach



Fig. 2. Micrographs of SAN – 1 wt% ND blends prepared by: "standard melt mixing" (1); melt-mixing in "spurt" regime (2); "colloidal-deposition" method (3); d) solvent method (4).



Fig. 3. Dimensional distribution of nanodiamond particles in SAN (1 %) for different mixing methods (optical diapason).



Fig. 4. Micrographs of composites SAN/1% of ND prepared by "standard mechanical mixing" (a), colloidal-deposition method (b) and in "spurt" regime (c).



Fig. 5. TEM images of composites SAN/1 wt.% ND obtained by standard melt-mixing (a) and mixing in "spurt" regime (b).

smaller particles of ND in polymer matrix was done via chemical blocking the surface functional groups presented in ND. Two reagents were tested for this procedure: trifluoromethansulfoacid (TFSA) and hexafluoroisopropanol (HFIP). In this case we cannot avoid organic solvent because dispersion of 1 g ND in 100 ml of hexane is treated by ultrasound, then 1 ml of TFSA or HFIP is added under permanent sonication. After deposition of particles, hexane was removed by decantation and 100 ml of acetone was added to deposit for washing. After subsequent agitation and centrifuging the powder was washed with distilled water and dried in exsiccator.

The most suitable method for combining modified ND particles with polymer is colloidal deposition since TFSA and HFIP could be added to inert solvent used as a medium for deposition of ND onto polymer grains. Visually, homogeneous by dimensions ND particles are absorbed by polymer surface. This method of compatibility will be considered again at analysis of mechanical properties of nanocomposites.



Fig. 6. Generalized polydispersity curve for SAN/1 wt% ND composite prepared in "spurt" regime.

3. Methods

3.1 Rheological properties

Both capillary and rotation equipment was used for measuring rheological properties: rotation rheometer "Rheostress 600" ("Thermo Haake", Germany) with operating units cone-plate and plate-plate, as well as capillary rheometer MV-3M of melt-indexer type (V.E.Dreval et al. 1995). As a rule, appearance of samples was analyzed visually after dismounting operating units after every experiment ("post-factum" mode).

Visualization of stream is very important for such heterophase systems as nanocomposites. The matter is that very often we think about stability of the distribution character at processing compared with precursors. But our experience shows that it is not true and shear field can change morphology of nanocomposite significantly. For this analysis the transparent cell of "lens-plate" allowing us to visualize shear stream in transmitting non-polarized and polarized light was designed and constructed. The scheme of this operating unit is presented in Fig.7a. Applied web-camera allows us to see evolution of morphology at flow. Knowing angular speed of plate rotation ω , curvature radius of lens (R = 50 mm), the gap between lens apex and plate h the shear rate was calculated

$$\dot{\gamma}(r) = \frac{2Rr}{r^2 + h}\omega\tag{1}$$

as a function of r. This dependence has maximum

$$\dot{\gamma}_{\max} = \omega \frac{\sqrt{2Rh}}{2h} \tag{2}$$

at $r = \sqrt{2Rh}$. If the gap is absent the dependence becomes by hyperbolic function:

$$\dot{\gamma}(r) = \frac{2R}{r}\omega \tag{3}$$

Actually, this apparatus scans a medium under investigation at constant angular velocity of plate.

In addition, based on this equipment the two-beam interferometer serving for visualization of stream morphology features for elastic polymer melts, solutions and nanocomposites, non-visible in transmitting light (details of modulation of refraction index of medium as a result of photoelasticity) was designed (Fig.7b).



Fig. 7. Scheme of equipment for visualization of stream in axially-symmetric shear field (a); scheme of interferometer (b). See explanations in text.

3.2 Rheo-X-ray

For rheo-X-ray measurements the following equipment has been used (S. Viale et al. 2005; Ruijter et al., 2006). Two glass coaxial capillaries with radii R_{out} =0.5 (outer, unmoved) and R_{in} =0.25 (inner, movable) and a length of ~10 cm combine the Couette cell (Fig.8a). The shear rate in the narrow gap, $\dot{\gamma}$ was calculated as

$$\dot{\gamma} = r \frac{d\omega}{dr} = \frac{\omega R}{R_{out} - R_{in}} = \frac{2\pi n (R_{out} - R_{in})/2}{R_{out} - R_{in}},\tag{4}$$

where ω is angular velocity and *n* is rotation speed (rpm). For the present geometry $\dot{\gamma} = 0,157n$.

The scheme of the experimental set up is shown in Fig. 8b. The Couette cell was adjusted relative to the collimator and 2D detector by means of the x,y,z-stage of the goniometer where using the alignment laser beam and video camera. The collimated X-ray beam can pass either through the centre axis of the Couette geometry (passing two gaps along the gradient axis) or tangential to the gap along the streamlines. In our experiments we mainly used the first option with the beam along the gradient direction. In all cases the differential X-ray diffractograms (background was capillaries filled with water) were detected. The diameter of the incident X-ray beam used was 0.5 mm.



Fig. 8. Image of the micro-Couette used in the experiment (a); scheme of experimental device for "rheo-X-ray" measurements (b).

The overall orientation can be expressed quantitatively in terms of the orientation parameter $\langle \overline{P}_2 \rangle$ that is calculated as follows. The intensity distribution can be described as

$$I = I_0 + Ae^{\alpha \cos^2(\phi - \phi_0)}$$
(5)

where φ is the azimuthal angle, α is a parameter characterizing the width of intensity distribution. Knowing α , we can calculate $\langle \overline{P}_2 \rangle$ as

$$\langle \overline{P}_2 \rangle = \frac{\int_{-1}^{1} P_2(\cos\phi) e^{\alpha \cos^2\phi} d\cos\phi}{\int_{-1}^{1} e^{\alpha \cos^2\phi} d\cos\phi}$$
(6)

3.3 Mechanical and thermomechanical properties

Mechanical properties of extruded samples of the circle cross-section were measured on tensile machine Instron 1122 at extension rate of 10 mm/min.

Notched samples of PSF/ND composites have been tested for Izod impact strength by standard method.

3.4 Tribological properties

By means of an original technique the sliding friction coefficient and wear resistance of composites relatively nichrome wire has been measured. Principle of tribometer action is the following: in the holder of horizontally located microdrill the tested sample (extrudate)

contacting with the counterface (nichrome wire, d = 50 mkm) on whole radius (angle of contact is 2π) was fixed. Rpm of the microdrill was chosen corresponding to the linear speed of wire sliding of 1 m/min. The friction coefficient was calculated using Euler's formula

$$S_0 = Se^{f\alpha} \tag{7}$$

where S_0 – loading, S – strain, f – friction coefficient, α - angle of contact of specimen with wire.

4. Results and discussion

4.1 Rheology and stream morphology

Development of morphology at flow (in-situ mode) was studied on model system: viscoelastic solution of PIB in cetane filled with rather large (d~80 mkm) monodisperse spherical particles of PMMA. For matrix solution normal stresses start to exceed tangential stresses (Weissenberg number, Wi > 1) at shear rate of 0.2 s⁻¹ as is seen from dependences of stresses and viscosity on shear rate (Fig.9).



Fig. 9. Dependences $\sigma(\dot{\gamma})$ - 1, $N_1(\dot{\gamma})$ - 2, $\eta(\dot{\gamma})$ - 3 for PIB solution in cetane.

This is important point where elastic response of solution becomes dominant. 5 % of PMMA microspheres were introduced to this solution, a drop of composition was placed in the center of plate and lens of the apparatus as shown in Fig.7a, and squeezed it up to formation of desired gap width (in this case h=200 mkm). Shooting via microscope with partially crossed polars was done just to see simultaneously morphology and optical anisotropy of a matrix at flow. A series of frames from a movie illustrating the evolution of morphology in axially symmetric shear field in time at angular speed of 1 rad/s is shown in Fig.10.

The initially chaotic distribution of PMMA spheres in PIB solution is gradually replaced by ordering of particles on a background of Maltese cross indicating on optical anisotropy of photoelastic matrix initiated by shear. Particles participate in a curve motion forming first



Fig. 10. Evolution of stream morphology for PIB solution filled with 5% of PMMA spheres. Time increases from a) to f).

short chains and then extended arches, and at last the closed circles. Ordering process looks like formation of chains with closed package of particles along streamlines. It is important to note that there appear alternating layers along radius enriched by particles. In other words, stratification of stream takes place and initially chaotic distribution of particles is replaced by their ordering. Since there is a gap between lens and plate, the radial profile of shear rate has a maximum. In the center the rate as well as the stress is equal to zero, then it increases up to a distance of 4.5 mm ($\dot{\gamma} = 10 \text{ s}^{-1}$), then decreases monotonically up to zero again. The vision area on frames is approximately 3 mm, and this means that on periphery of frames the shear rate is maximum ($\dot{\gamma} = 9.8 \text{ s}^{-1}$). In the central zone there is no ordering of particles, and chains of particles appear at a distance of 0.2 mm, at $\dot{\gamma} > 1 \text{ s}^{-1}$ and Wi > 5. The position of circles formed by particles is not stationary: circles increase the radius and slowly migrate to the periphery of operating cell.

So, large spherical particles arrange as concentric circles in the strong shear flow of viscoelastic polymer matrix. What will happen, if dimensions of particles will be essentially smaller and their shape will be not spherical? To answer this question the same matrix was filled with 7% wt of clay Cloisite Na+. Clay particles are anisotropic and appear birefringence, i.e., visually detected in polarized light a⁺ crossed polars. This composition demonstrates ordering of particles in strong shear flow ($\gamma > 1$ s⁻¹) forming arches and as a limiting stage – circles as well (Fig.11).

Observation in-situ mode allows us to see two kinds of motion: rotational and translational with subsequent formation of ordered circles. The ordering process starts in vicinity of lens apex, but the most regular circles are seen in the middle of vision area, while in periphery of cell where the gap is widening, a tendency only to arrangement of particles is observed. As in previous case, the developed morphology is not stationary – circles "are running" from the center to periphery. It is likely that the driving force of ordering are critical values of shear rate and stress that are maximum near the apex (more precisely at a distance of 0.35).



Fig. 11. Subsequent stages of regular morphology formation by 7 %wt of Cloisite Na+ particles in PIB solution. Time interval between frames is 10 min.

mm from the center at $h\sim 1$ mkm) and decrease along radius because of non-linear increase of the gap (Fig.12). Movement of circles is likely stipulated by gradient of normal stresses along radius generating driving force acting on a set of particles.

The developed morphology is stable and does not change at least several days. The picture shown in Fig.12 was taken after 24 hours stay the sample after formation of this morphology. It is seen that on a distance more than 4 mm from the center corresponding to shear rate \sim 1 s⁻¹, there are no circles. It is critical shear rate corresponding to the definite relation between elastic and viscous forces generating regular morphology formation. One of intrinsic feature of this picture consists in possibility of circle twinning that can be detected for the last circle closed to zone where capability of particles to regular arrangement disappears.



Fig. 12. Micrograph of composite based on PIB solution and Na-montmorillonite particles after 24 hours after circles formation accompanied with dimension scales and distribution diagram of shear rate. Arrow indicates twinning the circle.
As a starting point of the driving force of regular arrangement of particles in strong shear field, two approaches should be considered. The first one is based on hypothesis about structure transformation of polymer matrix influencing on particles location. The second one – on specific change of rates and stresses fields in presence in viscoelastic matrix of impurities or defects, such as solid particles.

For analysis of the first factor morphological pictures should be added by flow curves of heterophase compositions. As an example, corresponding data for SAN filled with natural and modified Na-montmorillonite are presented in Fig.13. In contrast with classical Einstein law postulating increase of suspension viscosity with volume fraction of solid particles, in our case the viscosity changes with filler content non-monotonically (Fig.13a). The lowest viscosity for systems with Cloisite Na+ is realized for 5% dispersion. It is strange that this effect is observed for all shear rates used. The effect is not caused by destruction of SAN during mixing procedure because neat polymer was subjected to the same temperature-shear rate-time action, as blends.

In the case of hydrophobic organoclay (Cloisite 20A) evolution of viscosity with filler content looks more natural: the viscosity increases with a filler content at low shear rates (up to appearance of yield stress) and decreases at high shear rates. By the way, similar dependence was obtained before for polypropylene-Cloisite Na+ system (Kulichikhin et al., 2000). It seems to us that a term "Non-Einsteinian viscosity" used in some publications (M.E. Mackay et al., 2003) is not correct because we deal with viscoelastic but not Newtonian medium, particles have anisotropic but not spherical shape, and viscosity measures at different but not at one shear rate. Sooner, there is sense to discuss specific dependence caused by small dimensions of particles, their specific interaction with matrix polymer (Jain et al., 2008) and capability to be oriented in shear stream, by non-natural conformation of macromolecules in absorbed layers, as well as partial intercalation of macromolecules into interspaces of layered aluminsilicates. Difference in behavior of hydrophilic and hydrophobic clays in the same matrix can be explained by specific interaction of nitrile groups with solid surfaces of various polarity and as consequence - by different degree of intercalation. Nevertheless, if to analyze dependences presented in Fig.13b, the decrease of viscosity with a content of clay at high shear rates domain is evident.

Clay particles are rather large in diameter (\sim 5-7 mkm) and small in a thickness (\sim 20-30 nm), i.e. they are anisometric and almost plain. Particles of ND are almost spherical, and diameter of individual particle is \sim 3-5 nm, but they are agglomerated. Traditional mechanical mixing procedure of ND with the same SAN leads to maximum distribution function localized at 1-2 mkm. Nevertheless, it is a filler with isotropic particles and their influence on SAN melt viscosity should be interesting, especially compared with anisometric clay particles.

Dependences of viscosity on shear rate for a set of these compositions are shown in Fig.14. In the field of low shear rates rotational rheometer was used, meanwhile for high shear rates field – capillary apparatus. In the whole range of shear rates (stresses) a decrease of viscosity with filling degree is observed, but viscosity minimum is located for ND content 0.5% and a scale of viscosity decrease is essentially less than for SAN-natural clay system (only 44% of SAN viscosity, but not ~6 times as for previous system).

It should be noted that experiments on capillary viscometer were carried out with capillaries of different 1/d (at the same diameter). Coincidence of data obtained on different capillaries confirms an absence of sliding.



Fig. 13. Dependences of viscosity on shear rate for SAN filled with hydrophilic (a) and hydrophobic clay (b). Content of clay: 0 (1), 5 (2), 10 (3) and 20% (4). T = 220°C.

To understand precisely an influence of particles dimensions on viscosisty, two series of formulations with the same composition steps have been prepared based on PSF matrix and nanodiamonds in traditional and "spurt" regimes. Corresponding dependences of viscosity on ND concentration are presented in Fig.15. For traditional mixing the effect of viscosity decrease at 1% of ND is prominent, while for compositions prepared via "spurt" regime it is absent, and monotonous increase of viscosity with amount of filler is observed.



Fig. 14. Dependences of viscosity on shear stress for SAN-ND compositions prepared via reference method. Dotted line – rotation rheometer, solid lines – capillary rheometer. ND content: 0 (1), 0.5 (2), 1.0 (3), 2.5 (4) and 5% (5).



Fig. 15. Concentration dependences of viscosity measured at τ =12.5 kPa for PSF-based composites, obtained by two methods.

Based on a series of experiments with different polymer matrices and fillers, the effect of viscosity decrease at definite content of a filler is not unique inherent for a few pairs polymer-filler only. Presumably, it reflects the common property of filled compositions with viscoelastic polymer matrix. The current tendency consists in more significant scale of this effect for large particles (agglomerates of nanoparticles) and weakening the effect with decrease of particles size. It can disappear as whole for nanosized particles. The effect takes place in the field of strong shear flow, i.e., in the same conditions that inherent for formation of the circle-like morphology. It is likely that both effects are interrelated and we can tell about decrease of viscosity with filling degree for stratified flows.

If a homogeneous melt will be placed in a cell of shear rheometer, in absent of sliding the angular momentum transfers homogeneously from the moving to stationary part (translation mode, Fig.16a). At presence in a melt of anisometric particles capable to rotate in shear field, the second mode of dissipation appears – rotational. At low shear rates superposition of two modes increases the hydrodynamic resistance of a system leading to viscosity growth (Fig.16b). In these conditions a laminarity of stream can be destroyed. However, at high shear rates localization of modes can take place and transition to stratified flow (formation of a circle morphology indicates on reality of this situation) where translation and rotational modes are concentrated in different layers (Fig.16c). We can expect decrease of mechanical energy dissipation and, consequently, decrease of viscosity.



Fig. 16. Scheme of transition from laminar flow of homogeneous system (a) to irregular superposition of translation and rotation modes (b), and to stratified flow (c) in heterogeneous system.

Formation of the circle morphology is typical as well for blends of incompatible polymers (Kulichikhin et al., 2001), and in this case drops of disperse phase should have low viscosity and be enough large (more than critical Taylor radius) to be extended in shear field to form closed circles. The viscosity of two-component blend is a sum of inputs stipulated by viscosity of components and their volume fraction. If we consider the effective viscosity of a homogenous multi-component system then the viscosity is often found to be given by a logarithmic rule of mixing:

$$\log(\eta) = \sum_{i} \phi_{i} \log(\eta_{i}) \quad \text{or} \quad \eta = \prod_{i} \eta^{\phi_{i}}$$
(8)

where the summation runs over all the volume fractions (ϕ_i) and viscosities (η_i) of the pure components. This sort of expression is commonly used to calculate the viscosity of homogenous polymer blends.

On the other hand, if to assume that a stratified system consisting of i layers exists, we obtain (Abramowitz & Stegun):

$$\frac{1}{\eta} = \sum_{i} \frac{\phi_i}{\eta_i} \tag{9}$$

It is worth noting that the effective viscosity of the stratified system (eq.9.) is invariably lower than for the homogenous mixture (eq.8.). Thus, if at definite conditions a transition from homogeneous (segmental) to stratified flow takes place, the viscosity should be decreased. As was seen the similar effect of viscosity decrease caused by stratification of stream can be observed at high shear rates for filled systems as well.



Fig. 17. Linear, geometric mean and harmonic mean viscosity averages for a two component system with viscosities of 10 and 100 (a.u.).

The resulting curves for the various rules of mixing are schematically shown in Fig.17 assuming viscosities of 10 and 100 respectively. When we now apply a fast shear flow on our material the overall dissipation will be higher for the homogenous system than for the stratified system. This means that the flow will act as a driving force to cause the system to phase separate into "high" and "low" viscosity bands. The low viscosity bands then reduce the effective viscosity of the whole system. In the present case of a polymer containing

nanoparticles the nanoparticles tend to accumulate in the fast flow so that the viscosity increase is effectively reduced via lubrication by the low clay content regions in the flowing system.

So, we have tried to prove that the effect of viscosity decrease can be caused by stratified flow of more-less large particles, that is why it is connected with morphological transformations of a heterophase system. But what is the driving force of regular morphology formation? Earlier, there were suggested two possible reasons: specific change of polymer matrix in strong flow and influence of particles on laminarity of flow. First of all, let us consider, what happens with individual polymer melt in strong flow.

If we will come back to Fig.9, it is possible to select four regions of shear rate corresponding to different rheological responses. Zone I corresponds to Newtonian behavior (the viscosity does not depend on shear rate and shear stresses are much higher than normal stresses). In Zone II non-Newtonian flow starts and this situation can be described as reversible destruction of fluctuation network of entanglements (the viscosity decreases with shear rate and shear stress growth in less extent than shear rate). In Zone II normal stresses become higher than shear stresses (this means that elastic response prevails). At last, Zone IV corresponds to "spurt" behavior (both components of stresses are almost constant).

In the case of capillary flow various kinds of irregularities appear on extrudate surface (Fig.18), in the case of rotational flow irregularities of stream (vortexes of elastic turbulence) start on periphery and pass to the center (Fig.19).



Fig. 18. Irregularities of polymer extrudate surface at increase of shear rate (from left to right).

However, there exists shear stress-shear rate window (pre-"spurt" region) where individual polymer melts appear regular texture. As an example, the surface of cohesion rupture of polycarbonate formed on pre-"spurt" regime realized on both parts after dismounting the operating unit cone and plate is shown in Fig.17. Besides, the new version of "spurt" phenomenon explanation as cohesion rupture but not adhesion slippage should be taken into consideration.

It is surprising, but we come across the circle-like or sooner the spiral texture again. Actually, the sample surface has spiral structure that in a distance looks like concentric circles. Moreover, formation of this surface proceeds via twinning the spiral (see spiral periphery in the bottom part of the picture).



Fig. 19. Irregular surface of polycarbonate in "spurt" regime realized in cone-plate geometry. Dotted line corresponds to "dimple" direction.

Formation of the spiral structure at high shear rates is possible to see directly in transparent cell. The micrograph of PIB melt in transmitting light with a sharp black boundary separating flow zone and the surface formed as a result of medium rupture is shown in Fig.20. The narrow zone of the surface close to flow region has regular spiral structure. Spirals are directed by such a way that they are going from flow region (defectless part in the center of sample). On the earliest stage of the spiral structure formation (Fig.20a) evolution of spirals proceeds via twinning of their period (arrows show doubling of furrows). With time (Fig.20b) spiral ridges transform to ring-like morphology.



Fig. 20. Subsequent stages of texture formation from spiral (a) to circular (b) for PIB melt. The distance between lines in figure b) is 1 mm.

To know what happens in the flow zone the optical interferometry was used. The interference pattern of the flow zone for polybutene melt in vicinity of lens pole is shown in Fig.21a. The regular texture becomes visible at angular velocity of a plate of the order of unit of rad/s as alternating light and dark bands spreading from the center to the periphery. In transmitting non-monocromatic light this zone remains transparent.



Fig. 21. Texture of polybutene in interference (a) and white light mode (b) in vicinity of rotation axis of the lens-plate cell at $\omega = 0.5$ rad/s (a) and 1 rad/s (b).

Comparison of Figs. 21 and 20, allows us to judge that spiral texture of the surface breakage on a periphery of stream is continuation of texture initiating in "transparent" zone (transmitting white light). Interference spiral structure appears as a result of modulation of refraction index due to photoelastic effect. At high shear rates (Wi>1) in polymer melt elastic stresses (reversible strains) appear that are visualized by optical interferometry. Dark fields correspond to extension, light ones – to compressive stresses. The dark "half-moon" region in Fig.21a corresponds to initiation of "spurt" or cohesion rupture of a melt. At increase of angular velocity up to 1 rad/s the regular instabilities appear visible in white light (Fig.21b). Effects described above are observed in strong flow where elasticity of polymer matrix becomes a dominant factor of its rheological behavior. The same time it is well-known appearance of instability or secondary flows may take place in viscous inelastic liquids (classical example is so-called Tailor vortexes forming in confined geometry as a result of inertial effects. What is a difference between inertial and elastic instability? We were lucky to observe a transition from one kind of instability to another one for very similar systems varied with different level of elasticity.

At shear flow of diluted aqueous dispersion of nanodiamonds in presence of non-ionic surfactant (Tween 80) the initially homogeneous dispersion is separating on a system of rotating radial formations formed by ND particles (Fig.22). These figures are very similar to Tailor vortexes (Larson, 1991), when inertial forces become to be dominant over viscous forces. Formation of vortexes starts in vicinity of the lens pole and they develop to periphery of stream that is similar to circles evolution considered above. The main distinction consists in direction of instability figures: longitudinally or transversally to shear.

One can see the transition from inertial instability to elastic one, if 1% of HPC will be introduced to aqueous medium of the same dispersion. The rather weak elasticity is enough for drastic change of stream morphology: instead radial structures concentric circles or spirals are forming. (Fig.23).

Thus, experiments carried out as with nanocomposite precursors, as with dispersions in Newtonian or weakly viscoelastic media, as with individual polymer melts indicate on formation of regular structures in strong shear flows. The main reason of regular structures development should be the intrinsic profile of elastic stresses and strains, i.e., their periodic modulation. That is why the profile of elastic forces in polymer melts and the texture of particles distribution in strong flows should be similar. This circumstance is decisive in the search of driving forces of ordering.



Fig. 22. Morphology evolution with strain in aqueous suspension of ND in presence of surfactant.



Fig. 23. Morphology evolution with strain in suspension of ND in 1% aqueous solution of HPC.

It is likely that the main factor of regular arrangement of particles is action on them of elastic forces from polymer matrix that itself becomes structured or textured in strong flows. Filler particles play a role of tracers reflecting stratified polymer flow.

4.2 Rheo-X-ray data

For complex liquids, such as liquid crystals, colloid systems, incompatible polymer blends, nanocomposite precursors combination of rheological testing with structural methods is a stable tendency now. Strong influence of shear rates and shear stresses distribution in intense shear on stream morphology has forced us to look more detail on structure transformations on a level of crystalline lattices. Together with Dutch partners (Makarova et al., 2010) a series of experiments was carried out at the Delft University of Technology

where a combination of Couette cell and X-ray scattering cell was developed. Since the most fruitful results should be obtained on structure active objects, the aqueous LC solution of HPC was used as a matrix and crystalline Na-montmorillonite as a filler.

For choice of HPC solution concentration, the phase diagram of HPC-water system was constructed by means of optical microinterference method (Malkin et al., 1983); Makarova, 2007). According to this method, interacting substances are placed in side-by-side manner in the wedge gap and the diffusion profile is registered as evolution of interference fridges inherent to each component. In equilibrium state the terminal concentrations are taken as limits of reagents solubilities at different temperatures and used for constructing the phase diagram.

As an example, the interference patterns at two temperatures are presented in Fig 24a. Along the diffusion zone at 29°C four different sections are observed that correspond to the traditional phase sequence (from left to right) inherent to solutions of stiff-chain polymers: isotropic (I), biphasic (II), LC (III) and CS (IV), as well as the exact location of boundaries between them. With increase of temperature the interference pattern changes dramatically. Sections I and II disappear and the sharp border identified as amorphous phase separation appears. Based on these data, the phase diagram of HPC-water system was drawn (Fig. 24b) (Kulichikhin et al., 2010), reflecting superposition of two kinds of phase equilibria: amorphous (binodal with low critical mixing temperature) and LC equilibrium, theoretically predicted in (Flory, 1956). With increase of polymer concentration isotropic solution (I) transforms to liquid crystalline (LC), and this transition proceeds through biphasic region of coexisting of I and LC phases. At extremely high content of HPC formation of crystal solvate (CS) phase is possible. Of course, the most interesting solutions as matrices for rheo-X-ray study are anisotropic, and to make the final choice the concentration dependence of viscosity was considered.

As a rule, the viscosity decreases with appearance of LC-phase due to change of flow mechanism from segmental movement to displacement of domains which easily orient in shear field (Kwolek, 1972; Papkov et al., 1974). The same situation takes place for HPC solutions. The corresponding dependence of viscosity on HPC content is shown in Fig 25.

As is seen, the viscosity minimum appears at HPC content of 50% corresponding to biphasic region. This concentration was chosen as a matrix for dispersion with clay. By the way, presence of clay does not influence the location of equilibrium lines of the phase diagram, but leads to increase of viscosity at low shear rates almost proportionally for whole concentration diapason.

Before analysis of difractograms at flow, we need to know features of X-ray scattering of neat HPC and clay powders. These data are shown in Fig.26.

For HPC scattering maxima at 2Θ =8.8 and 20.2° are inherent. Unfortunately, main reflexes of clay are located in vicinity of these angles: at 6.8 and 19.7°. The first one is the basal reflex corresponding to interspace distance in layered crystalline structure. It changes the position depending on intercalation (penetration) of any species into clay structure. Partially, its position depends on water content shifting with increase of moisture level to smaller angles. That is why we can expect change of basal reflection location for aqueous solutions.

First of all, the neat solution was suffered to shear in Couette cell with different shear rates with registration of diffactogram. Corresponding results are shown in Fig. 27. HPC orientation is expressed as a strong reflex on meridian of diffactogram at 2Θ =6.1⁰ and becomes prominent at shear rate higher than ~20 s⁻¹.



Fig. 24. Microinterference patterns of interdiffusion zone of HPC-water system at two temperatures (a), and phase diagram based on these data (b).



Fig. 25. Concentration dependence of viscosity for HPC solutions and composites on their base measured at shear rate 0.25 s⁻¹ and ambient temperature.



Fig. 26. Diffractograms of Na-montmorillonite and HPC powders.



Fig. 27. 2-D diffraction patterns of 50% HPC solution exhibiting the dependence of orientation on shear rate at 0 (a), 28.2 (b) and 226.1 s⁻¹ (c).

Distribution of intensity in azimuthal angles (Fig.28) show that weak initial orientation caused by loading of solution into the gap between two capillaries at flow rotates on 90°, i.e., LC solution becomes oriented along the shear direction.

Dependence of order parameter calculated on shear rate is shown in Fig.29. The initial value of $\langle \overline{P}_2 \rangle$ (0.16) is stipulated by orientation at loading and under action of shear its value increases to 0.66.

In the case of nanocomposite precursor we need to separate reflexes inherent to HPC and clay. Looking at diffractograms in 2 Θ angles (Fig. 30), one can see that basal clay reflex in aqueous solution is shifted to ~3.2^o, while the reference HPC reflex remains at 6.6^o, so, it is easy to distinct them. In the rest state the HPC reflex is rather weak and this means that major fraction of HPC molecules is connected with clay due to absorption and intercalation.



Fig. 28. Distribution of azimuthal intensity of the strongest reflex of 50% HPC solution at different shear rates.



Fig. 29. Dependence of order parameter on shear rate for 50% HPC solution.

With increase of shear rate the redistribution of intensities between reflections inherent to clay and HPC occurs, and this process can be caused by release of HPC molecules from clay force field. The microphase separation takes place. Details of structure change might be understood from analysis of X-ray patterns of 50% HPC solution filled with 5% of Namontmorillonite presented in Fig. 31.

As is seen, in initial state "the loading effect" leads to superposition of reflexes inherent for HPC and clay on equator of difractogram. With increase of shear rate these reflexes become separated: the HPC reflex moves on meridian, and clay reflex remains on equator. These displacements are expressed clearly on difractograms in azimuthal angles (Fig. 32).



Fig. 30. Evolution of diffractograms along 2Θ angle for 50% HPC solution containing 5% of Na-montmorillonite with shear rate.



Fig. 31. 2-D diffraction patterns of 50% HPC solution filled with 5% of Na-montmorillonite on shear rate equal to: 0 (a), 113.0 (b), 282.6 (c) and 471.0 s⁻¹ (d).

After engaging "equilibrium positions", evolution of orientation for each component proceeds in different way. For HPC already at low shear rate the orientation angle becomes 180^o but its intensity changes with increase of shear rate non-monotonically. The maximum orientation for clay is observed after loading, while the beginning of flow leads to decrease of basal reflex intensity. With increase of shear rate this reflex may oscillate between 245 and 270^o, but its intensity increases monotonously.

Dependences of order parameters (separately for HPC and clay) on shear rate (Fig. 33) indicate on existence of region of critical shear rates (around 300 s⁻¹) where both parameters suffer deviation from smooth evolution. For HPC in this region the order parameter demonstrates wide minimum, and for clay the value of order parameter becomes dependent on flow time (or total strain). In the first moment after flow starts up it decreases sharply, but with increase of strain it comes back to high values. This feature led to necessity of detail research of X-ray patterns evolution in time at highest shear rate of 471 s⁻¹ to understand the strength of developed structure. These results are presented in Fig. 34.

As is seen, at deformation time between 70 and 75 min the clay reflex changes the position and moves from equator to meridian. At higher observation time this situation does not



Fig. 32. Distribution of azimuthal intensity of 50% HPC solution filled with 5% of Namontmorillonite at different shear rates for HPC and clay separately.

change. Therefore, at strain of the order of 2.10⁶ the catastrophic transformation of clay particles orientation takes place. This phenomenon is reflected on the dependence of order parameter on time (Fig. 35) that jumps down in this region.

If to look on evolution of difractograms in 2Θ angles, it is evident the redistribution of intensities between reflexes 6.6 (HPC) and 3.2° (clay): the first one decreases in favor of the second one (Fig. 36). Moreover, the last reflex moves to position of 3.1°. This situation is opposite to observed evolution of difractograms with shear rate (Fig. 30) where intensity of the 6.6° reflection increases and 3.2° decreases. This means that clay structure suffers drastic transformation at definite strain. What kind of is this transformation?



Fig. 33. Evolution of the orientation of HPC and clay with shear rate for 50% HPC solution filled with 5% of Na-montmorillonite.



Fig. 34. 2-D diffraction patterns of 50% HPC solution filled with 5% of Na-montmorillonite at 5 (a), 70 (b), 75 (c) and 115 min (d) after reaching the shear rate of 471 s⁻¹.



Fig. 35. Dependences of order parameter of HPC and clay for suspension under consideration at prolonged deformation at shear rate of 471 s⁻¹.



Fig. 36. Diffractograms of 50% HPC solution filled with 5% of Na-montmorillonite at prolonged deformation at 471 s⁻¹.

First of all, let us accept that so strong clay reflex (in all versions of our experiments) reflects macro-ordering of clay platelets. This means that they form extended formations similar to chains. In the case when clay reflection is located in equator it should be long sequences oriented by axis perpendicular to platelet thickness along the shear direction. Such situation is very similar to columnar mesophase that looks like stacks of coins. This structure becomes stable at shear rates corresponding to circle-like morphology formation described above and observed in transparent unit (see comparison of hypothetic arrangement of particles in cell Couette and in cone-plate unit in Fig.37). The concurrence of two kinds of mesophases can lead to smooth decrease of HPC orientation and to dependence of clay orientation on time (pronounced decrease of orientation on start-up stage) evident from Fig.33.



Fig. 37. Hypothetic arrangement of particles in Couette cell (a) and in cone-plate unit (b). As is seen from dependence of viscosity on shear rate regular ordering proceeds at shear rate of \sim 300 s⁻¹.

After prolonged strain at high shear rate the clay reflex is turned on 90° and displaced from equator to meridian, the columnar structure should be destroyed as a result of flow instability and accumulation of heat due to viscous friction, and probably be converted to the version of discotic mesophase (Schmidt et al., 2000) with orientation of the axis transversal to platelet thickness along the vorticity axis (in our case it coincides with the long axis of capillaries forming the Couette cell). This situation is drawn schematically in Fig. 38. Clay particles become less oriented and their order parameter decreases sharply at this time.



Fig. 38. Scheme of probable transformation of columnar structure to discotic one.

Thus, morphological and structural data are interrelated. In strong shear flow when reversible deformations become dominant something happens with a system leading to regular arrangement of clay particles as on optical level, as on a level of crystalline cell. What does it mean "something", how to touch the possible driving forces of regular ordering?

We will not touch the theoretical background here in details, since the paper is experimental that is more important now in the field of nanocomposites area. But the analysis of literature and our own data suggest that high deformation rates in flow of viscoelastic micellar colloid and polymer systems lead to the flow-to-rubber-like transition. It is the limit of the strong non-linear behavior of elastic liquids. As a result, instability and different effects demonstrating formation of ordered structures were observed. The conception describing the behavior of such a kind based on the refusal from continuum field approach and developing a discrete model which consists in elastic rubber-like grains is proposed and discussed in (Semakov & Kulichikhin). This is a model of behavior of an elastic liquid in the strong non-linear region of shear rates and stresses. The behavior of the structure elements in this model is determined by their elastic deformations in shear flows (transition from a spherical to ellipsoidal shape of grains and their orientation) and by elastic interaction of these elements due to their collisions. The computer simulation demonstrated that this model really describes the consequence of elastic instability as the chaos-to-order transition and creation of experimentally observed regular structures. This is rather rare case when investigation of nanocomposite gave a food for the new vision of polymer behavior at intense shear strains in spite of a role of particles not more than tracers detecting and contrasting the texture of polymer matrix.

From position of processing conditions of nanocomposites based on rheological principles, it is more important to consider in short mechanical properties reached by declared in this Chapter approaches.

4.3 Mechanical properties

The best tensile properties were achieved for composites obtained by melt-mixing in "spurt" regime. Maximal values of SAN, PSF (neat polymers were treated in the conditions of composites preparing) and the nanocomposites are presented at Table 1.

Parameter	Polymer matrix	ND content, wt.%	Value
Young modulus, G _{max} , GPa	SAN	0	2.12
		2.5	2.95
	PSF	0	1
		5	1.9
$\begin{array}{l} Tensile \ strength, \\ \sigma_{max}, \ MPa \end{array}$	SAN	0	46
		0.5	65
	PSF	0	103
		0.25	150
Elongation at break, $\epsilon,$ %	SAN	0	3
		0.5	3.6
	PSF	0	32
		0.5	74

Table 1. Tensile properties of polymer-ND composites obtained by melt-mixing in "spurt" regime.

The basic tensile properties of the composites were improved significantly. The optimal filler content is 0.5% by weight. Increases in Young modulus and strength indicate that nanodiamonds are acting as reinforcing agents in the polymer matrix by homogeneous redistribution of load between bulk polymer and absorbed layers around ND particles. The decreasing of mechanical characteristics of the composites obtained by a standard meltmixing, observed in several papers including this one, can be explained by presence of a considerable quantity of the large agglomerates acting as a defects of the system.

Composites PSF/ND has been tested for impact strength. Fig.39 shows the influence of ND concentration and method of composite fabrication on impact strength.



Fig. 39. Izod impact strength of PSF/ND composites manufactured by different ways.

As it seen, already 0.5 wt.% of ND results in increase of impact strength almost in 2 times. Composites prepared by standard melt-mixing possess essentially the worst properties. This can be attributed to poor uniformity of the ND distribution in the polymer matrix.

4.4 Tribological properties

The effect of ND addition to PSF on sliding coefficient of friction is shown in Fig.40. Nanocomposites with ND exhibits a much less steady state coefficient of friction compared with the neat PSF.



Fig. 40. Friction coefficient of PSF and PSF-ND nanocomposites. Wear conditions: sliding velocity -1 m/s, duration – 15 min.

Fig.41 shows the micrographs of the abraded surface of polysulfone and polysulfone nanocomposites (scaled up area of extrudate). By incorporating ND the wear is significantly reduced. Hard nanodiamond particles provide protection and prevent the polymer matrix from severe wear.



Fig. 41. Micrographs of the worn surfaces of the PSF-ND nanocomposites: neat PSF (a), PSF/1 wt.% ND (b), PSF/2.5 wt.% ND (c), PSF/5 wt.% ND (d). Wear conditions: sliding velocity -1 m/s, duration – 15 min.

Brief review of mechanical properties we would like to finish by characteristics of nanocomposites containing modified ND. The corresponding data are shown in Fig.42.



Fig. 42. Concentration dependences of the tensile yield stress for the neat and modified ND.

Essential improvement of mechanical characteristic is observed for ND modified by hexafluoroisopropanol. Namely this reagent leads to blocking carboxyl and carbonyl groups on the surface of ND particles. The similar effect takes place also for elastic modulus. Diminishing of interacting groups on the surface can be reached as correct choice of mechanical mixing regime, as chemical modification. However, due to its simplicity the first way looks more attractive.

5. Conclusions

The main focus of this Chapter was targeted on novel approaches to compatibility of particles with polymer matrices and detail analysis of rheology-morphology interrelationships. Rather attractive method of mixing based on knowledge of rheological behavior of polymers at high shear rates was proposed and studied. The major fraction of ND around 40 nm and absence of agglomerates of micron dimensions allow us to recommend this method for industrial application. For successful processing of nanocomposite precursors interrelationships between rheological properties and stream morphology is extremely important and depending on the task, it is possible to obtain either chaotic or regular distribution of filler particles. These data were obtained by combining rheological and optical or structural methods. Hypothesis over the main driving force of particles ordering based on regular elastic instability of polymer matrix causing ordering of particles was proposed. Mechanical characterization confirms the strong influence of dimensional homogeneity of particles on final properties of nanocomposites.

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Nanocomposite Electrolyte for PEMFC Application

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1. Introduction

Fuel demand is predicted to increase by 6.3% by each year, in particular the motor vehicle sector where is expected to increase by 41% per year. Gas generated from burning fossil fuels produce emission that cause global warming effect as perceived from the parameters such as (i) increase in global temperature, (ii) global climate change phenomena and (iii) the melting of the ice caps.

One effort to overcome the effects of global warming is by replacing fossil fuels with hydrogen fuel. Hydrogen fuel and fuel cell technology had been proven able to minimise the production of toxic flue gases produced by combustion of fossil fuels. Hydrogen fuel is one of the first order candidate to replace fossil fuels because the combustion of hydrogen produce only electricity and water without the emission on of CO_2 , NO_x , SO_x and volatile organic compounds. In addition, hydrogen as a raw material can be renewed and could be harvested from multiple processing methods.

Some countries have tried to produce renewable fuels with a large capacity as would be done by China by 2020 where it is expected to produce 20% of the renewable energy while New Zealand at 70%, Brazil has been producing bio-fuels on large scale and U.S. bio-fuel have been supplied from corn. U.S. and Japan have reserved the hydrogen as a substitute for fossil fuel. It is estimated that hydrogen fuel to be economical by 2050.

Fuel cell technology will be one of the appropriate technologies to convert hydrogen into electric energy when hydrogen is continuously supplied. Fuel cell would be able to replace fossil-fuelled engine with higher efficiency and expected to produce minimum or no pollutants and have been developed in order to reduce the problems of green house gas effect produced through the combustion of fossil fuel.

1.1 Proton Exchange Membrane Fuel Cell (PEMFC)

Fuel cell is a power generator that convert hydrogen and oxygen via electrochemical reaction into electrical energy with, the thermodynamic efficiency as high as about 60%, comparing to the conventional engine which is only 30% efficiency. Electric power is resulted from electrochemical oxidation reaction of hydrogen molecule at an anode surface and resulted in the movemet of the electron (e⁻) and proton (H⁺). In addition, reduction of

oxygen molecules takes place at cathode surface and produce oxygen ion (O^{2}). Protons from the anode are delivered to the cathode through the electrolyt membrane when electron moves through the external circuit left the system to be used as an electric power. The electrons then reenter the cathode surface. Where, oxygen ions, electrons and protons will electrochemically react to produce water molecules.

The reactions taking place at the cathode and anode surfaces are indicated by reaction mechanisms in equation (1) to (3) (Gyenge, 2005). The result of the power conversion is water which make PEMFC device an environmentally friendly electric power generator (Kong et al., 2002).

Anode
$$2H_2 \longrightarrow 4H^+ + 4e^-$$
 (1)

Cathode
$$O_2 + 4e^- \longrightarrow 2O^{-2}$$
 (2)

Cathode $2O^{-2} + 4H^+ + 4e^- \longrightarrow 2H_2O$ (3)

Among the different type of fuel cells, PEMFC is the most interesting to researchers and industries as the power device in the automotive. Due to this cell can be adjusted with the size of required power, and can be used for various power generator devices.

1.2 Basic component of proton exchange membrane fuel cell (PEMFC)

PEMFC components consist of two electrodes, i.e. anode and cathode, separated by the electrolyte membrane. The anode is supported by anode gas diffusion layer (GDLA), while the cathode is supported by cathode gas diffusion layer (GDLC). This cell is sandwiched by the bipolar pate and current collector, end plates and external circuit to connect the anode and the cathode (Mahreni, 2009). The single cell schematic configuration of PEMFC, is presented in Fig. 1 (a) & (b) bellow.



Fig. 1. Schematic PEMFC component (a) and schematic operation (b) of the PEMFC system. (1) End plate (EP), (2) Current collector (CC), (3) Bipolar plate (BP), (4) Gas diffusion layer (GDL), (5) Electrode, (6) Proton electrolyte membrane (PEM). The schematic of PEMFC power generation is shown in Fig. 1 (b). (http://id.images.search.yahoo.com/search/images)

The function of GDL is to support the catalyst. As well as the gas distributor via the porous layer as a way the water molecule would exit from the system. It also acts as electron conductor through the carbon particles. The microstructure of the GDL greatly affect the

fuel cell performance because this is the site that establish the electron transfer resistant from and to the electrolyte surfaces (Park et al., 2004).



Fig. 2. An example of a plate.

An example of bipolar plate in Fig. 2 there are four main functions of the bipolar plate namely (i) as a flow field of fuel, air and coolant, (ii) as a separating cell unit from other cell unit in a stack, (iii) as a conductor of current from a cell unit in the stack and as (iv) as a support of a series of membrane-electrode assemblies (MEA) (Lee et al., 2007).

Catalyst layer is made up of Pt/C which is used as the electrode to accelerate the reaction of hydrogen oxidation on the anode surface and oxygen reduction reaction on the cathode surface.

The improvement of PEMFC had been carried out to minimize catalyst concentration and increasing catalyst resistance to CO. The efforts have been done of reducing the catalyst particles to nano size in order to increase the surface active area of the catalyst. The other attemt that have been done to increase the resistancy of the catalyst to the CO poisoning is increase the operating temperature of PEMFC. At higher temperature CO molecules less adsorb to the catalyst surface make the life time of the catalyst is increase to.

Perfluorosulfonic acid (PFSA) membrane, such as Nafion, is the polyelectrolyte most widely used in PEMFCs because it exhibits excellent inherent properties of up to about 90°C in terms of the proton conductivity, mechanical stability and chemical inertia. Smitha et al., 2005 have reported the disadvantages of Nafion membrane, as follow (i) the price is very expensive (\$ 700/ m²), (ii) requires a humidification device, and (iii) limited usage it a low temperature. The PEMFC development in future needs electrolyte membranes having characteristics including (i) high conductivity to support a fast current by minimizing a potential loss caused by internal resistance and moreover caused by H⁺ ion transfer resistance through the membrane, (ii) isolator for electron transfer, (iii) adequate mechanical and chemical resistance and electrochemically stable under operating condition, (iv) impermeable against oxygen and hydrogen, and (v) cheap.

Power resulted by a fuel cell is known from resulted current density and voltage. This cell performance is influenced by the electrochemical reaction rate in anode and cathode. The electrochemical reaction rate is influenced by many factors, among them are the thermodynamics, kinetic, ion and mass transfer (Gynge, 2006).

The temperature effect on thermodynamic and kinetic parameters can be explained by reaction parameters involved in the power generation, where (i) standard exchange current density (i_0), (ii) equilibrium voltage (E_{rev}), (iii) Tafel slope (b) and (iv) electron transfer rate coefficient (α).

Standard exchange current density, i_0 is a basic property of an electrode which can be defined as oxidation or reduction rate at the equilibrium condition which is represented as current. The current at the equilibrium condition states that oxidation and reduction rates are in the equilibrium. There is no theory that can be used to calculate standard current density at a certain system and must be calculated by experiment.

Value of standard exchange current density depends on some parameters related to electrode properties, i.e. type of catalyst metal, characteristic of catalyst surface and pollutant concentration at the catalyst surface. Other than electrode characteristic, temperature is also greatly influence to the value of standard exchange current density. Standard exchange current density (i_0) is increasingly when the temperature increased. Beatti et. al. reported that the value i_0 of Pt/Nafion 117 increases from 2,8x10⁻¹⁰ A/cm² at the temperature of 303 K to 3,71 x10⁻⁹ A/cm² at the temperature of 343 K. The value of i_0 at Pt-membrane surface other than Nafion (BAM 407) is reported increased when the temperature increases from 8,80x 10⁻¹¹ A/cm² at 303 K to 4,38x10⁻¹⁰ A/cm² at 343 K. Increasing the value of i_0 at a higher temperature shows that the catalyst activity getting increase.

Thermodynamic equilibrium voltage (E_{rev}) is the maximum voltage which may be resulted when 1 mol of water is resulted by $\frac{1}{2}$ mol of oxygen and 1 mol of hydrogen at a certain condition. Equilibrium voltage is influenced by temperature and partial pressure of hydrogen and oxygen at the catalyst surface. Equation (4) shows $V_{thermodynamic}$ H₂/O₂ = V_{cell} , maximum i.e. the maximum voltage or equilibrium voltage at standard condition (pressure of 1 atmosphere, temperature of 25 °C and reactant activity = 1).

$$V_{\text{cell, maximum}} = E_c - E_a = 1.229 \text{ volt}$$
(4)

Generally, the reaction takes place in a non standard condition. Cell voltage (V_{cell}) at a non standard condition is calculated based on Nerst equantion. The expanded Nerst equation is a model equation used in the PEMFC system by Gyenge (2005) as in equation (5).

$$E = E^{0} + \frac{RT}{2F} \ln \left(\frac{P_{H_2 P_{02}^{0.5}}}{P_{H_2 O}} \right)$$
(5)

E and *E*⁰, R, T, F, *P*_{*H*₂}, *P*_{*O*₂}, *P*_{*H*₂O} respectively are cell potential and open circuit potential, gas constant, temperature, faraday constant, partial pressure of hydrogen, oxygen and water. Resulted cell voltage always smaller than equilibrium voltage. The decreasing voltage from equilibrium voltage is caused by polarization. Polarization taken place in the PEMC comprises polarization of catalyst activity, polarization of electron and proton transfer, and polarization of mass transfer. Equation of polarization model can be expressed as equation (6) (Baschuk et. al. 2000).

$$E = E_0 + b\log i_0 - b\log i - Ri - \gamma \exp(\omega i)$$
(6)

The resulted power of a cell is *P* as in equation (7).

$$P=EI$$
 (7)

where $E, E_0, i, b, R, \gamma, \omega, P$ respectively are cell voltage (V_{sel}), open circuit voltage (V_{ocv}), current density (*i*), Tafel slope, electron and proton transfer resistance (*R*), mass transfer resistance (γ), fitting parameter (ω) and power (*P*). The open circuit voltage is a electrical

potential difference between cathode and anode when there is no electric current. The Tafel coefficient depends on temperature empirically may be expressed as equation (8).

$$b = \frac{-2.3RT}{\alpha nF} \tag{8}$$

Where F, R, α are respectively Faraday constant, gas constant and constant of electron transfer in the electrode, and *n* is the number of electrons involved in electrochemical reaction. Equation (8) shows that Tafel constant is influenced by temperature, where as higher the temperature the higher the Tafel constant (Berger 1968), (Zhang et. al. 2006).

It is probably concluded by the researchers that the Tafel slope and oxygen reduction reaction will increase when the temperature increases at the range of a low current density. At a high current density, the Tafel curve does not depend on the temperature. Another advantage which can be reached at a high temperature condition is that rate of CO absorption greatly slower than the rate of hydrogen, so the limit CO content in the fuel may reach 100 ppm (Zhang et. al. 2006; Xu et. al. 2006).

Principally, the hydrogen resulted from the reforming process that use as the fuel for PEMFC today, generally has high CO content, have impurities about 200 ppm which requires purification device before hydrogen can be used as a fuel. To make the resulted hydrogen from this reforming process able to be used as a fuel directly without CO purification, the operating temperature has to be increased (Yang et al., 2001) up to 130 °C, where platinum catalyst may resist against CO content up to 1000 ppm. Hence the choice to increase the cell performance of the fuel cell in the future is to increase the operating temperature.

1.3 The problem statement

The obstacle of high temperature operation is the membrane shrinking, that would lose the mechanical strength and increase hydrogen and oxygen permeability. The hydrogen and oxygen penetrated through the membrane and co exist at the catalyst-membrane surface create exothermic reaction thus increasing the temperature on one side or a hot spot at the membrane surface. The temperature in that hot spot location will increased that could easily membrane damage. The shrinking of Nafion membrane or (PFSA) group, would normally takes place at high temperature and low relative humidity condition which is accompanied by decreasing membrane conductivity to proton. The Nafion 115 conductivity decreased by decreasing water activity at the temperature between 80 to 140 °C (Yang et al., 2004).

The research is still undergone in order to PEMFC may compete the existing machine potentials. Among the researches which had been carried out in commercializing PEMFC include (i) developing anode catalyst which resisted to CO, for example using metal alloy such as Pt-Ru/C, Pt-Ru/C (nanotube), in order to be used with CO content in the hydrogen reach > 50 ppm, (ii) using other type of membrane that cheaper than Nafion membrane or modifies the Nafion membrane that has high conductivity at low relative humidity (Mahreni et al., 2009).

1.4 Nafion membrane

Perfluorosulfonic acid (PFSA) membranes (e.g. Nafion) is not suitable used as electrolyte of high temperature and low relative humidity PEMFC due to anisotropic membrane swelling that occurs when the membrane is pressed between the electrodes, which provoke

irreversible conductivity decay (Alberti et al., 2007). The possibility to modify physical and chemical properties of a polymer by dispersing inorganic nanoparticles in the polymeric matrix (Ramani et al., 2005; Adjemian et al., 2002) encourages the development of proton conducting composite membranes suitable for PEMFCs that could work at temperatures above 100°C and low relative humidity.

Therefore, the research focuses on membrane performance improvement and suitable as electrolyte of high temperatures and low humidity PEMFC.

1.4.1 Understanding the structure of the Nafion membrane

The structure of Nafion ($C_7HF_{13}O_5SC_2F_4$) membrane is shown in Fig. 3 and 4. These figure shows the Nafion structure and Nafion cluster respectively (Smitha et al., 2005; Hamnett 2003).

Nafion is a poly electrolyte composed of tetrafluoroethylene (CF₂-CF₂) (TFE) segment which is the main chain of the polymer and perfluorosulphonic vinyl ether (PSVE) ((CF₂-CF(OCF₂-CF(CF₃)-CF₂-CF₂-SO₃H) as chain side. The backbone of polymer is non-polar or hydrophobic which is the fluorocarbon chain that provides the mechanical strength and heat resistance properties to Nafion. The side chain of the Nafion polymer that its end is sulphonic group (SO₃H), is polar (hydrophylic) and could transfer protons. The amount of x for Nafion membrane is 6.5 (Klein et al., 2005).



Fig. 3. Chemical structure of Nafion membrane.



Fig. 4. Nafion cluster (Hamnett, 2003).

Micro structure of Nafion membrane consists of crystalline and ionic phase. Ionic group is SO_3H -functional group which is surrounded by primary water molecules. Some ionic group with the size of (2 to 4) nm form a one unit cluster. Between one cluster and other clusters are connected by a narrow channel, which has size of 1 nm. Ionic group and the channels

sizes depend on the amount of existing water in the membrane. The size of the cluster and channel comparable with water content in the membrane (Jiang Yu Li & Sia Nemat-Nasser. 2000).

The existing water molecules and the electro osmotic drag in the membrane will increase proton mobility and the protons (H⁺) of sulphonate group (SO₃H) will escape. Protons that have been separated from the sulphonate group, may coalesce with H₂O molecules in the form of hydronium (H₃O⁺) and oxonium (H₂O₅⁺) ions are transferred through the membrane.

The water that fills Nafion polymer pores around the hydrophilic section is recognized as the primary water. The primary water consists of three molecules of water for every sulphonate group. If the amount of primary water has been fulfilled, the excessive water fills the main chain and side chain of pore size (4 to 10) nm. The water that fills these pores is called the secondary water. If the water content in the membrane is adequate for primary hydration, the proton transfer through the membrane is equal to the proton diffusion rate through water molecules. It can be concluded that the proton conductivity is proportional to the water molecules content in the membrane. Therefore, the higher the water content the higher the proton conductivity and vice versa.

Another characteristic that determines the membrane conductivity is water uptake rate (WUR). Water uptake rate (WUR) can be defined as the maximum water content that can be absorbed by the membrane on the certain temperature and relative humidity condition. The water uptake rate is associated with membrane permeability properties against polar solvents for example water or alcohol. The higher the WUR is the higher the conductivity and vice versa (Mahreni et al., 2009).

Considering that the water content in the membrane is very critical determining proton conductivity. So the water control in hydrogen fuel cell requires special attention because water is continuously produced by the reaction at the cathode. Water is also carried by hydrogen and oxygen from the outside of the cell as a humidifier to hydrogen and oxygen.

1.4.2 Model of proton transfer in the Nafion membrane

Two models that have been proposed and would be able to explain the mechanism of proton transfer through Nafion membrane is Kreur, 1996 describing the vehicle theory and second model presented by Grotthuss who proposed the theory of protons hopping (Ramani et al., 2005).

The vehicle model assumes that the moving protons will always be accompanied by water molecules in the form hydronium (H_3O^+) or Jundel ions ($H_2O_5^+$) and eigen ions ($H_9O_4^+$) (Pivovar, 2006). Hydronium molecules diffuses from one ionic group to the other ion group in the membrane polymer matrix. Transfer of hydronium ion caused by the concentration difference between ionic group. Diffusion of the hydronium ion causes the back diffusion of water molecules occure in the opposite direction with the direction of hydronium ion diffusion. Furthermore, water molecules otomatically may bind a proton to form hydronium ion again, and by the substitute of protons can be through the membrane polymer matrix continuously.

Proton transfer rate is in line with hydronium ion transfer rate through a group of water molecules. The ion transfer illustrated as a proton hopping between the ionic groups (SO_3H) can be presented in Fig. 5 and 6 below.

Proton hopping model illustrates that the water molecules are not moving (still) remains in place. Proton hops from one ionic group (SO₃H) to the other ionic groups through the water

media which remained in place. Proton hops caused by the original arrangement (reorientation) of sulphonate group from asymmetry form to symmetry form. In hydrated conditions, the change of asymmetry to symmetry occurred faster. This condition causes the activation energy of proton hopping becomes lessen and causing the transfer rate of the proton faster. If the water content is low then the time required by a sulphonate group to return to symmetrical form is slower and proton transfer to be slow (Ramani et al., 2004).



Fig. 5. Mechanism of proton transfer in the Nafion membrane in accordance with (a) the vehicle theory and (b) proton hopping theory.



Fig. 6. Protons hopping in the Nafion membrane.

High water content in the membrane also causes the size of the channel that connects a group of ionic and other ionic groups will get larger and encourage water diffusion more rapid. In accordance with the vehicle theory which explains that when a water diffusion is fast, the transfer of protons also fast.

2. Composite electrolyte membrane based on hydrocarbon-inorganic materials

Sulphonated hydrocarbon polymers have been studied to replace Nafion by reason of cheaper and higher heat resistance compared to Nafion membrane. Hydrocarbon components that have been used are sulphonated polysolphone (PSF), polyetersulphone (PES), polyetereterketone (PEEK) (Ayad et al., 2005), poly(imides) (PI) and poly (4-penoxibenzoil-1,4-phenilene) (PPBP). Hydrocarbon membrane is stable at high temperature. Aromatic polyimides has been synthesized by (Genies et al., 2001) and shows a high conductivity but the structure of main chain of the polymer easily be hydrolyzed. Sulphonated polybenziimidazole (PBI) has been produced by several researchers and has been used as an electrolyte in the PEMFC. The grafted polybenziimidazol (PBI) with sulphopropil unit shows conductivity of 10-3 S cm⁻¹ at the temperature region of (20 to 140) °C and better than Nafion at the same condition, but if the PEMFC operating temperature is

increased up to temperatures of above 100 °C, the membrane loses the sulphonate acid group because of hydrolysis reaction.

The weakness of hydrocarbon electrolyte membrane is the main chain of sulphonated hydrocarbon polymer that less hydrophobic and the sulphonated acid group less acidic and more polar. Therefore, the water molecules inside the membrane is dispersed in the polymer nanostructure and causes at the saturated humidity (100% RH) the water diffusion rate of Nafion membrane is higher than the hydrocarbon membrane. The higher water diffusion rate of Nafion at 100% RH has meaning conductivity of the Nafion membrane at saturated condition higher than hydrocarbon membrane.

3. Modified PFSA membrane

PFSA membrane modification is lead to produce membrane that has high stability at high temperatures (80 to 120) °C and at low humidity.

The main objective of the membrane modification is to make the membrane could to transfer the proton without water molecules or make the membrane as self humidifier membrane by introduce the dopan component that could transfer proton via proton hopping mechanism. This effort was less successful, so effort to improve the Nafion membrane is still continue with the target to improve water management by adding a hygroscopic component and high conductivity such as silica and inorganic materials. This effort is quite successful because by entering silica component and or strong acid can reduce the membrane thickness and the membrane is stable at low humidity, and easily control the water content in the membrane (Adjemian et al., 2002). The resulting composite membrane can absorb water more than the pure Nafion.

4. Composite membrane of Nafion-SiO₂-HPA

Organic-inorganic composite membrane consist of organic membrane of Nafion and inorganic component of SiO_2 -HPA, SiO_2 -SiWA, SiO_2 – SiMoA having a high conductivity than Nafion membrane. In this case, the role of and SiO_2 as HPA immobilizer so HPA would be exist fix in the Nafion polymer matrix.

4.1 Heteropolyacid (HPA).

One type of HPA is phoshotungstic acid ($H_3PW_{12}O_{40}$, PWA) which has been successfully used as filler of electrolyte membranes used in PEMFC and can also be a catalyst for the reaction of CO and O₂ to produce CO₂. CO is always in small amounts in the hydrogen fuel. Structure of molecule HPA consists of complex Bronsted acid that joined with polyoxomethalate anion (heteropoly anion) in which the HPA has the basic bond structure of metal-oxygen for forming octahedral units. Such composition is known as the Kegin composition of heteropoly anion.

FTIR analysis results show difference of the bond among oxygen atoms in the HPA component. The difference of the bond is shown by the spectrum peaks at different wave number. Bonding of phosphate and oxygen (P-O_a) is indicated by the occurrence of spectral peaks at wave number of (1079 cm⁻¹) meanwhile the bond of tungstic and oxygen is shown by W-O_b-W (edge-shared octahedral of Kegin units) a sign by peak at wave number of (893.09 cm⁻¹) (Ramani et al, 2005).



Fig. 7. Kegin structure of atomic oxygen in the $H_3PW_{12}O_{40}$ 6 H_2O (Irene et al., 2009; Bielanski & Lubanska, 2004).

Peak of the W-O_b-W is occurred at the wave number of 821 cm⁻¹. The W-O_d-W (terminal oxygen) peak is occurred at the wave number of 981.81 cm⁻¹, W-O_c-W (corner shared octahedral of Kegin units) is occurred at wave number of 765 cm⁻¹. HPA crystal consists of anions, cations surrounding the anions are H⁺, H₃O⁺ or ion H₅O₂⁺ ion and crystal water. Crystal water can be separated by heating. The water release process which can be reversed can be seen by the change in crystal volume. In contrast to the system established by the zeolyte, the HPA Kegin structure is easy to move (mobile). Water and all polar solvents can enter and leave the HPA crystal. HPA crystal properties is a very important as a difference phase catalyst. Solid HPA is acidic which stronger than the solid acid such as SiO₂, Al₂O₃, H₃PO₄-SiO₂, HX, HY, or zeolyte. HPA is very stable at high temperature. The decomposition temperature of the PW, SiW, PMo and SiMo, respectively, are 465 °C, 445 °C, 375 °C and 350 °C. Decomposition is occurred because of the loss of acid properties.

4.2 Silica dioxide (SiO₂)

Silica in the form of organo-silica tetraethylorthosilicate (TEOS) is more often used as precursors of inorganic materials to modify the Nafion membrane as compared with titanium (Ti) or zirconium (Zr). Viewed from the rate of hydrolysis and condensation reactions, the silica alcoxide is easier to control compared with titanium isopropoxide and zirconium alcoxide (Ramani, et. al. 2006). Zirconium is very reactive so to control the reaction requires the inhibitor component (Show et al., 2006; Ramani et al., 2004).

Tetraethylorthosilicate (TEOS) or Si $(OC_2H_5)_4$ is the component that has four groups of ligand. Ethoxide (OC_2H_5) is a ligand that reacts easily through hydrolysis and condensation reaction using water in an acid environment, alkaline or neutral.

4.3 Parameters that influence the properties of Nafion-inorganic composite membrane

Composite membrane properties are affected by many factors, especially inorganic content, methods and conditions that determine the physical-chemical properties and electrochemical properties of the membrane. Physics-chemical properties include microstructure, heat resistance, mechanical resistance, morphology and structure of chemical bond. Electrochemical properties include conductivity, membrane permeability to gas, ion exchange capacity (IEC), and water uptake rate (WUR) (Ramani et al., 2004).

4.3.1 Effect of the chemical properties to the micro structure of composite membrane

The physical-chemical properties of organic and inorganic component strongly influenced to the micro structure and electrochemical property of resulted composite membrane. Due

to the chemical and physical properties of component determines the interaction between the component in the reaction system especially the kind of bonding between the both components. In the synthesis of organic-inorganic composite, there are two types of bonding occurred, i.e. physical bonding and chemical bonding. The physical bonding is weak, for example, van der Wals bonding and moment dipole bonding. The composite membrane resulted by physical bonding usually easy to form inhomogeneous phase because aggregate forming between inorganic particles and the aggregate will deposit and separated from its organic phase. The composite membrane which is synthesized by chemical bonding has a strong bonding between both components for example by covalent or electrostatic bonding and the interaction between components is strong and homogenous. The strong bonding may prevent of forming aggregate of inorganic particles so the phase separation between both components does not occur and produce the composite with homogenous structure. Resulted membrane by chemical bonding, beside having a nano composite structure, it also has high mechanical resistance (Ramani et al., 2005).

In special case for the synthesis the composite membrane using sol-gel process, it needs the basic component from metaloid group, i.e. Si, Ti, Zr, Al in the form of organometallic because the metalloid component in the form of organometallic easy to hydrolyze with water and alcohol to produce silanol. Where the silanol may react with inorganic component via chemical bonding (Mauritz, 1998). The component resulted from hydrolysis reaction then is condensed to produce inorganic polymer matrix. Then cross link bonded inorganic polymer matrix with organic polymer so the interaction of both components is strong in the form of cross link bond structure between organic polymer chain and inorganic chain. Meanwhile, to increase conductivity, it needs strong acid, such as heteropoly acid (HPA), i.e. PWA, SiWA, WO₃ and SiMoA. In this research, the metalloid is used as a immobilizer of acid component, i.e. PWA, by electrostatic bonding between PWA ion and OH group of silanol, so PWA may stable in the matrix of Nafion polymer. Silanol also binds with SO₃H cluster of Nafion by hydrogen bond (Haobold et al., 2001; Bhure et al., 2006). Hydrogen and electrostatic bonds among the three components are desired may produce the composite that interaction between both component in the molecule level so may prevent the aggregate formation of inorganic component and prevent separation of organic-inorganic phase. Then produce homogenous composite membrane with have the nano scale structure. The reaction mechanism of silanol, PWA and SO₃H are present bellow.

Hydrogen bonding occurs between silanol group and sulphonate molecules of Nafion when electrostatic bonding occur between the silanol and PWA ion. The reason of using tetraetoxiortosilicate (TEOS) as a silicate source is because TEOS reactivity is controllable at low temperature condition and it cheaper than titanium and zirconium and easily provided makes TEOS is used as PWA immobilizer in the organic-inorganic composite membrane.

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$$\begin{bmatrix} (CF_2CF_2)_n (CF_2CF) \\ (OCF_2CF)_m (OCF_2CF_2SO_3H^+) \\ Nafion 112 CF_3 Hydrogen bonding (9)$$

Si(OC_2H_5)_4 + H_2O \longrightarrow ESi(OH) + C_2H_5OH
TEOS Water Silanol Ethanol

Electrostatic bonding

$$=\operatorname{Si}(\overset{\cdots}{O}H) + H_{3}PW_{12}O_{40} \longrightarrow \left[=\operatorname{Si}OH_{2}\right]^{+} + \left[H_{2}PW_{12}O_{40}\right]^{+} (10)$$
Silanol PWA

4.3.2 Effect of solvent properties to the properties of composite membrane

The structure of the composite strongly depend to the properties of solvent used in the synthesis. In the synthesis, organic-inorganic composite membrane may use non polar, polar protic or polar aprotic solvent, depends on the polarity of the inorganic-organic component. For polar organic component, it may use protic polar or aprotic polar solvent. The protic polar is a polar solvent and produces hydroxyl [OH-1] ion in the solution. When the aprotic polar is polar solvent, it does not produce hydroxyl ion in the solution. Examples of protic polar are of alcohol group, and the aprotic solvent such as dimethyl formamide (DMF), dimethyl sulphoxide (DMSO), dimethyl acetamide (DMAc) and tetra hydrofurant (THF). Basic choose of solvent properties is based on consideration that the reaction between organic and inorganic components takes place. Specifically in the synthesis of organicinorganic composite membrane using Nafion as an organic component and TEOS-PWA as an inorganic component, it is inappropriate to use polar protic solvent, because its produces hydroxyl ion which may be interact with SO₃H of the Nafion. When the interaction occur between sulphonate group with hydroxyl [OH-1] from the solvent, the synthesis between sulphonate and SiOH does not occurred and the separation of organic phase (Nafion) and inorganic phase (SiOH-PWA) takes place. The second consideration is the solvent boiling point. The solvent is selected to have a boiling point almost the same as the glass transition temperature (T_g) , instead of its organic component (Ramani et al., 2005). For example, the glass transition temperature of Nafion is in the range of 130 °C to 140 °C, depends on water content in the membrane. DMF solvent has the boiling point of 153 °C, DMSO is of 189 °C, THF is of 66 °C and DMAc is of 166 °C. Selected to be DMF because of having the boiling point closer to Tg than Nafion so DMF is the solvent used. The DMF have been used by many researchers in the synthesis of organic-inorganic composite membrane (Staiti et al., 2002; Ramani et al., 2005; Shao et al., 2004).

5. Preparation of Nanocomposite Nafion-SiO₂-PWA membrane by using solgel method

Fabrication method is a critical factor that influence the resulting composite membrane structure. To produce a composite membrane having the desired properties requires the appropriate selection method. The method to synthesize the Nafion/metal alcoxide/HPA composite membrane will follow the given process, namely, the impregnation, the dispersion and finally the in-situ sol-gel method.

This research is carried out to produce Nafion-SiO₂-PWA membraneby using sol-gel methode using 5% Nafion solution as organic material in the isopropylalcohol (IPA) solvent. Nafion solution is left in the fume hood to evaporate the solvent and produce the solid Nafion. Further the solid Nafion is dissolved in dimethylformamide (DMF) it becomes 5 wt.% Nafion solution in DMF solvent. The next step is mixing the tetraetoxyortosilica (Si(OC₂H₅)₄, TEOS) and phosphotungstic acid (H₃PW₁₂O₄₀, PWA) to Nafion-DMF solution
and stirred for 6 hours to produce homogeneous solution. Then the solution is poured into a Petri dish and left in the room condition during 24 hours to release trapped air bubbles. The membrane in the form of a thin layer is carried out by heating the solution in an oven at a temperature of 80°C so that all the solvent evaporates and the process was continued at a temperature of 140 °C, to produced a transparent membrane. The resulting membrane removed from the dish by way of boiling it in the water. After that, the membrane is washed using 0.5 M sulfate acid solution at a temperature of 80 °C for one hour, washed in water at a temperature of 100 °C and washed again in 3% of hydrogen peroxide solution at a temperature of 80 °C for one hour and washed again in water until the rinsed water becoming neutral then dried at room temperature and then dried at a temperature of 80 °C in vacuum. Furthermore, the physical-chemical properties are analyzed using FTIR, TGA, SEM, TEM, UV-VIS, EDX, XRD, WUR and FCTS. The membrane produced then is given the name: NS10W, NS15W, NS20W.

6. Result and discussion

Nafion-SiO₂-PWA composite membrane is a mixture of three components, namely Nafion, TEOS and phosphotungsten acid. Nafion is the main material of organic compound membrane and the PWA is an inorganic compound material that is added to the polymer to increase the Nafion conductivity. TEOS is immobilizer in order PWA is not to be separated from the Nafion polymer matrix. Preliminary analysis had been conducted to determine the maximum content of PWA in the silica pores. This step is done to ensure that the PWA cannot be separated from the Nafion-SiO₂-PWA mixture. Analysis is performed using solgel method by mixing TEOS solution, water and methanol with the mole ratio (TEOS: water: methanol = 1:4:4). The location of PWA Chrystal in the SiO₂ surface is determine using X-ray spectrometer (XRD). XRD analysis is also carried out on SiO₂ crystal and PWA, in the pure state to compare the XRD pattern neither the PWA Chrystal is in the silica pore or in silca surface. The result of XRD analysis to the mixture of SiO₂-PWA shows that the maximum PWA content in the silica in the wt. ratio of PWA/SiO₂ is 0.45.

The Nafion-SiO₂-PWA composite membrane is synthesized from Nafion, TEOS and PWA solution using the maximum ratio of PWA:TEOS 0.4. Preliminary analysis to determine the temperature of solvent evaporation, annealing temperature and annealing time needs to be done to produce a composite membrane which has transparent properties. Physics-chemical properties are analyzed using SEM, EDX, FTIR, TGA, UV-VIS, WUR and TEM.

6.1 Determination of solvent evaporation temperature

Solvent evaporation temperature is influence to the structure of resulted composite membrane because the temperature determines the reaction rate between the functional groups of organic and inorganic component. Specifically in the synthesis of Nafion-SiO₂-PWA composite membrane, at a low temperature, the reaction rate is very slow so it may not provide silanol molecule in the adequate amount to react with sulphonate and PWA ion. The research that had been carried out by (Ramani et al., 2005; Staiti et al., 2001; Zoppi et al., 1998) found that evaporation temperature of the solvent is different depends on the properties of reactant and solvent used, where part of them is used at low temperature (Zoppi et al., 1998), intermediate temperature (80 to 100) °C (Ramani et al., 2004), and high temperature above 100 °C (Staiti et al., 2002) or closed to boiling point of the solvent. Effect of evaporation temperature on the composite membrane properties has not been

investigated yet. Therefore, based on previous research results it can be concluded that there are three temperature levels of evaporation of the solvent, i.e. the evaporating temperature that far below the solvent boiling point, closed to solvent boiling point and above the solvent boiling point. Determining of solvent evaporating temperature is always related to solvent function itself in order to increase the reaction rate among involved components in the reaction. It is recommended that the solvent does not evaporate before the reaction taking place because one of solvent function is shortening the distance between reacted molecules so the reaction takes place faster. If the solvent evaporates before the reaction taking place then the reaction will not be occurred, instead the separation of organic-inorganic phase is occurred.

In this experiment solvent evaporation temperature is changed between the temperature (30 °C, 80 °C and 140 °C) so that all the solvent evaporate, and the solid membrane in the form of thin film is produced. Then, the membrane is heated at a temperature of 140 °C for 10 hours so as to produce the Nafion-SiO₂-PWA composite membrane. The characterization result directly shows that the resulted membrane at solvent evaporation temperature of 80°C has transparent property, meanwhile the resulted membrane at the solvent evaporation temperature of 30 °C and 140 °C are translucent. Therefore, based on that observation, it can be concluded that the best solvent evaporation temperature is 80 °C. The appearance of transparency shows that the resulting composite membrane has a homogeneous structure and does not apply separation of organic-inorganic phase (Zulfikar, 2005). The appearance of transparency also indicates that the composite membrane structure is already in the nanometer scale.



Fig. 8. Appearance of the resulted composite membrane using sol-gel method at solvent evaporation temperatures of (a) 30 °C, (b) 80 °C and (c) 140 °C (Mahreni et al., 2009)

Optically transparency is used as the initial measurement on the homogeneous phase formation from organic-inorganic phase. As can be seen in Table 1, the resulted composite membrane at low evaporation temperature of 30 °C has the translucent characteristic and cracked and the obtained composite membrane at the temperature of 80 °C has properties of transparent and does not crack. The membrane can easily forms a thin film, meanwhile at the high evaporation temperature of 140 °C it produces the porous composite membranes and uneven thickness. Therefore, it can be concluded that the circumstances the best solvent evaporation temperature is 80°C. Similar results were obtained in the synthesis of Nafion-SiO₂ composite membrane that was reported by (Adjemian et al., 2001). This can be explained that the solvent evaporate temperature is very influential to the formation reaction rate of silanol group (SiOH) resulted through the hydrolysis reaction of TEOS in Nafion-TEOS-PWA solution.

Silanol group compound is necessary to react with sulfonic functional groups of the Nafion which is by hydrogen bonding (Haobold et al., 2001) and by reaction with a group of PWA

ions through electrostatic interactions (Bhure et al., 2008). Thus, chemical interaction can apply to among organic compound (Nafion), inorganic compound (silanol group) and PWA. Chemical interaction among all of these compounds will prevent phase separation among all of the three compounds and produces a composite having a strong bond among the existing components in the system and is homogeneous. At low temperatures, the possibility of the formation of silanol group is slow so chemical interaction among the three compounds is not applicable and possible occurs the phase separation. Phase separation among the three compounds produces membrane that has opaque appearance as shown in Fig. 8 (a). Therefore, the higher the temperature, the faster the reaction and the formation of silanol group compounds is also faster.

If viewed from the solvent evaporation rate, the higher the temperature, the faster the solvent evaporation. The solvent acts as a medium that can increase the collision factor between the reacted reactants. By the existence of solvent, reaction rate becomes faster and prevent the formation of inorganic particle aggregate involved in the reaction. When the solvent evaporates before occurring the reaction between Nafion-Silanol group compound and silanol group-ion PWA, reaction the three components will be slower due to the solvent medium has evaporated and the possibility of occurring the phase separation by inorganic particles that form aggregates and settles. Aggregate formation led to the greater particle size and heavier, therefore the deposition process can not be circumvented. Deposition of inorganic particles causes separation of organic-inorganic phase and causes the resulted membrane being translucent. At temperature of 80 °C, hydrolysis reaction of TEOS compound is occurred faster so it can form silanol group bonds immediately. Silanol group is adequately available to form bonds with the sulfonic group and PWA ions to produce a Nafion-SiO2-PWA composite. Rapid interaction between these three materials can avoid the occurance of phase separation between inorganic compounds and organic compounds that eventually produces a homogeneous composite. Hydrogen bonds between the silanol group and sulfonic and electrostatic interactions between the silanol group and PWA ions encourage the formation of membrane in the nanometer level because the lasting interaction phase is in molecule level. This can be analyzed through the membrane properties that is synthesized at a solvent evaporation temperature of 80 °C that are transparent as shown in Fig. 8 (b). Meanwhile, at the high solvent evaporates temperature of 140 °C, the increase in solution viscosity is very fast which makes resistance of interaction between the silanol group compound and sulfonic group and PWA becomes larger. This condition also causes occurring the phase separation and the characteristics of the resulting composite membrane at high evaporation temperature is also translucent and porous as shown in Fig. 8 (c) and Table 1.

Solvent evaporation temperature	Physical characteristic	Other visual observation
30 °C	Translucent	Crack
80 °C	Transparent	Flat
140 °C	Translucent	Porous

Table 1. Physical observation of Nafion-SiO₂-PWA (NS15W) composite membrane at various evaporation temperatures of solvent on constant annealing temperature of 140 °C and annealing time of 10 hours.

By the analysis result shown in Fig. 8, it can be concluded that the solvent evaporation temperature of resulting composite membrane which is transparent and homogeneous is at a temperature of 80 °C. Meanwhile the resulting composite membrane at the solvent evaporation temperature of 30 °C and 140 °C is not homogeneous and the phase separation between organic and inorganic is also occurred.

6.2 Determination of annealing temperature and time

In this case, the temperature factor must be adjusted to the properties of organic materials, especially glass transition temperature (T_g) of the Nafion. At the temperature that closed to the glass transition temperature of the organic component. Meanwhile above the glass transition temperature it is possible to change of physical and chemical properties of its organic component and it will be able to damage the Nafion structure. So needs to be studied further in order to obtain the appropriate casting (solvent evaporation and annealing) temperature, which can produce membranes that are not fragile, easily formed into a thin film so easy to use as the electrolyte in the PEMFC (Ramani et al., 2005).

Annealing is an important stage of the process especially in the synthesis of composite membranes, the field of materials and metallurgy. By this process, material properties such as hardness and strength may change due to changes in the microstructure of these materials (Jesse et al., 2007). Annealing process is usually done by heating at a certain temperature adjusted to the desired material properties, followed by cooling slowly. According to the thermodynamic, annealing is occurred because the absorption of atoms in a solid material made of solid material more towards the equilibrium state. In this state, an amount of heat is needed to provide power that may break the bond to have atomic absorption quickly.

Annealing process commonly used in the synthesis of semiconductor materials, where the process is carried out on thin silica and varnish materials usually boron, phosphorus or arsenic (Ar). Varnish materials can absorb into the crystal lattice at a particular location and can produce a change in the electrical properties of semiconductor materials.

The transparency of the composite membrane is obtained from annealing treatment for 10 hours at a temperature of 140 °C. Annealing in the synthesis of composite membranes Nafion-SiO2-PWA is the process whereby occurring the strengthening of organic polymer and inorganic polymer tissues. Polymerization occurs in organic materials where the monomer (ionomer) Nafion is joined with other monomers to form a series of polymer chains.

Annealing Temperature (°C)	Vaporization temperature (°C)	Annealing time (hour)	Membrane property	Other visual observation
80	80	10	Translucent	Flat
100	80	10	Translucent	Flat
140	80	10	Transparent	Flat

Table 2. Physical observations of Nafion-SiO2-PWA (NS15W) composite membrane at various annealing temperatures.

Meanwhile, polymerization also applies to the inorganic component of the silanol group compounds (SiOH) who joined the cluster of other silanol group to form a silane bond (Si-O-Si). The second polymerization process of organic-inorganic compounds run

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simultaneously to form a cross-linking structure and during the polymerization process will be occurred the reaction between the silanol group-sulfonic group and silanol group-ion of PWA throughout the process. The result of the three components reaction is expected to be the composite compounds which are arranged through inorganic polymer chain and organic polymers that cross-linked and forming organic-inorganic hybrid polymer tissue as predicted in Fig. 9.



Fig. 9. Prediction of Nafion-SiO2-PWA composite membrane molecule structure

6.3 Effect of ratio of TEOS-PWA/Nafion to the physical-chemical properties of the Nafion-SiO₂-PWA composite membrane

Inorganic components are hygroscopic and have high conductivity can be added to the Nafion membrane with the aim to increasing the water uptake rate of the membrane. It is expected that water diffusion rate through the membrane increase with inorganic material content.

The effect of inorganic material content can be seen from the microstructure and mechanical strength of the membrane. The higher content of inorganic components in the composite membrane, the higher mechanical strength, but when the inorganic content to be raised, the membranes become brittle. The Nafion-SiO₂ composite membrane with SiO₂ content higher than 30 wt. % produces a brittle composite membrane so cannot be used to be formed into thin film (Ramani et al., 2004).

The parameter studied is the influence of the TEOS:Nafion ratio on physics-chemical properties of the composite membrane. The ratio (weight/weight) ranges of TEOS:Nafion used are 0.1 (NS10W); 0.15 (NS15W) and 0.2 (NS20W). The physical-chemical properties is analyzed using SEM, TGA, FTIR, EDX and UV-VIS. The result of direct observation of the composite membrane is obtained on solvent evaporation temperature of 80 °C, annealing temperature and time are respectively of 140°C and 10 hours and the mixture ratio of PWA:TEOS is 4:10 (weight/weight) and shows the resulted Nafion-SiO₂-PWA membrane is transparent. Analysis result is found that when the ratio (TEOS-PWA):Nafion in the composite membrane increases, value of water uptake rate and thermal resistance also increases. Dissociation temperature of a sulfonic groups of pure Nafion membrane is 323.20 °C when the dissociation temperature of the Nafion-SiO₂-PWA membrane type NS10W, NS15W and NS20W respectively, are 353.53 °C; 368.75 °C; and 348 °C.

The water water uptake rate of pure Nafion membrane is 26.52 wt.% compared to water water uptake rate with the Nafion-SiO₂-PWA composite membrane type NS10W, NS15W and NS20W respectively, are 30.25 %; 33.43 % and 32.72 % by weight. Thermo gravimetric analysis results also show that the content of inorganic residue components of P, Si and W in the composite membrane NS10W, NS15W and NS20W are respectively 2.31 wt. %, 2.61 wt.% and 6.16 wt.%. The surface structure and the cross sectional of all the resulting composite membrane is homogeneous. The elemental analyze result of the P, Si and W components are bound to the Nafion polymer matrix. Analysis of XRD shows the components of P, Si and W are in all the resulting composite membrane and can be concluded that the inorganic components added into the Nafion structure such as Si (silica), P (phosphorus) and W (tungstic) cannot be separated even though the membrane is washed using a solution of weak acids and bases.

6.4 Physical observations

Optical sighting is an acceptable method and appropriate in approximation of distribution levels of inorganic phase in the organic polymer matrix and an easy method to determine the distribution of organic-inorganic phase in polymer matrix for organic-inorganic composite materials. If the composite material is transparent, it means that the inorganic phase is well-dispersed in nano-scale in the polymer matrix and formed phase equally between the organic polymer and it inorganic. If phase separation occurs, the composite membrane formed will look blur and not transparent. This situation will affect themechanical strength of the resulting membrane (Zulfikar, 2005). The physical properties of synthesized composite membranes at the solvent evaporation temperature of 80°C, the

annealing temperature of 140°C, annealing time of 10 hours with the ratio of TEOS:Nafion of 0.1; 0.15; 0.2 and 0.3 (weight/weight) and were labeled as NS10W, NS15W, NS20W and NS30W respectively present in Table 3 show that all of the resulting composite membranes are transparent.

Membrane type	Physical property	Space property
N112	Transparent	Flat (no crack)
NS10W	Transparent	Flat (no crack)
NS15W	Transparent	Flat (no crack)
NS20W	Transparent	Flat (no crack)
NS30W	Transparent	Crack

Table 3. The physical properties of Nafion membrane (N112) and composite membranes synthesized in the solvent evaporation temperature of 80°C, annealing temperature of 140°C, and annealing time of 10 hours.

These show that the phase separation is not formed and the inorganic phase distribution is uniform on every part of the organic phase in the nano-scale in the organic polymer matrix (Kong et al., 2002). To demonstrate the nanostructures have been formed from the composite membrane, the analysis is done using a UV-VIS to determine the membrane spectrum obtained in percent of emission against the wavelength in the range of between 200 nm to 700 nm.

6.5 Observation of transparency of the composite membrane using UV-VIS

Analysis of the transparency is carried out to distinguish the transparency level of the pure Nafion membrane and NS10W, NS15W and NS20W composite membranes. Analysis is performed using a spectrometer (UV-VIS-NIR-LAMDA-900/10/N102290) in the wavelength range of 200 nm to 700 nm. UV-VIS produces radiance percentage data (% T) versus wavelength as presented in Table (4) and Figure (12).

Wavelength	Radiance percentage (%T)			
(nm)	N112	NS10W	NS15W	NS20W
700	94,243 372	94,059 81	93,871 49	92,863 29
600	94,032 063	93,469 25	93,117 25	91,454 16
500	93,804 864	92,794 81	92,833 12	90,251 51
400	93,154 372	91,039 36	91,477 39	85,717 02
300	90,881 045	85,479 23	88,317 53	7,963 876
200	52,937 81	50,554 18	47,864 28	0

Table 4. UV-VIS analysis results on wavelength range of (200 to 700) nm for the N112, NS10W, NS15W and NS20W membranes.

The data of transmission such as those found in Table 4. and Fig. 10 show that if the wavelength is specified, the higher concentrations of inorganic components contained in the composite membrane, emission decreases. The decreasing of emissions is due to the size of inorganic particles become increasingly larger when concentration of inorganic components in the membrane increases (Kukovez et al., 2002; Wang et al., 2007).

Quantitative relationship between the percent emission and particle size has been conducted by many researchers (Khanna et al., 2005) using empirical equation model that relates among the emission, film thickness and the absorption constant which is expressed by equation 6 (Apparacio et al., 2005; Mahreni et al., 2009).

$$T = A \exp\left(-\alpha d\right) \tag{11}$$

where *T*, *A*, α , *d*, respectively, emission on the maximum absorption ($T_{\lambda max}$), constant (A = 1), absorption constant and thickness of the membrane. By using equation (6) and Table (4) with the membrane a thickness is set at (70 ± 5) µm, α for each membrane can be calculated as listed in Table (5).



Fig. 10. UV-VIS spectra of N112, NS10W, NS15W and NS20W membranes in transmission (%T) versus wavelength (nm) (Mahreni et al, 2009).

_	Membrane	2 (nm)	Transmission	a
	(µm)	$n_{\rm max}(nn)$	(T)	(cm-1)
	N112	200	0.529	92.22
	NS10W	200	0.505	97.45
	NS15W	200	0.478	105.44
	NS20W	300	0.079	361.53

Table 5. Constants of N112 membrane absorption and composite membranes on the thickness membrane of 70 μ m.

Table 5 shows that when the concentration of inorganic component in a composite membrane increases then the absorption constant of the membrane (α) will increases. By using a model which is written by equation (6), (7) and (8), band gap energy (E_g) of composite membrane can be calculated quantitatively.

$$ahv = D(hv - E_g)^n \tag{12}$$

$$E_{g,nanocrystal} = E_{g,bulk} + \frac{\pi^2 h^{*2}}{2R^2} \left(\frac{1}{m_e} + \frac{1}{m_h} \right)$$
(13)

$$h^* = \frac{h}{2\pi} \tag{14}$$

Where *h* is Plank's constant (6.6 x 10⁻²⁷ erg sec), E_g is energy band gap (eV) and n is a constant for the energy band gap directly or indirectly, $E_{g,nanocrystal}$, $E_{g,bulk}$, *h*, *R*, m_e , m_k respectively are pure Silica energy band gap (1.1 eV), Plank's constant and the particle size, the electron mass ($m_e = 1.08 m_o$) and the mass of the hole ($m_h = 0.56 m_o$) of silica particles. The energy band gap is used to calculate the size of inorganic particles in the composite membrane by using equation (8) and (9) (Singh et al., 2006; Xu et al., 2008; Khanna et al., 2005; Mahreni et al., 2009).

The result of UV-VIS analysis of all membranes is shown in Table 5 and Figure 12, N112, NS10W and NS15W membranes have maximum absorption at a wavelength of 200 nm. The percentage of emission membrane of N112, NS10W and NS15W at a wavelength of 200 nm is 0.529; 0.505 and 0.478. The maximum absorption of NS20W membrane occurs at a wavelength of 300 nm. At a wavelength of 300 nm, the percentage transmission of NS20W is 0.079. By that information and equation of (6), with A = 1 and 70 μ m of membrane thickness = 0.07 mm, absorption constant of each membrane can be determined and as in Table 5. The energy band gap is calculated using the constant absorption contained in Table 5 and extrapolate curve in Figure 16 in the (Mahreni, 2009), energy band gap can be determined and are in Table 6, along with energy band gap of pure silica reported by (Garrido et al., 2004) as comparison of energy band gap of silica components in the composite membrane (Eg, nanocomposite) and pure silica (Eg, bulk).

This study			Garrido et al., 2004	
Membrane	Eg (eV)	Particle diameter	Eg (eV)	Particle
		<i>(nm)</i>		diameter (nm)
NS10W	2,75	2,1	2,3	2,1
NS15W	2,5	5,13	2,11	3
NS20W	2,4	5,32	1,5	6

Table 6. Diameter of SiO_2 particles in the NS10W, NS15W and NS20W composite membranes as a function of energy band gap.

Table 6. shows if the content of inorganic components increase in the composite membrane, the particles E_g will decrease and the particle diameters will increase. This phenomenon proves that the higher content of inorganic components, the larger particle size that will be formed. This is because the higher concentrations of inorganic components will facilitate the formation of aggregates (Garrido et al., 2004). To measure the real particle diameter of inorganic compounds in the composite membranes, analysis is continued using transmission electron microscopy (TEM).

6.6 Chemical structure of composite membranes by using FTIR

Analysis of the chemical structure of composite membranes is conducted using FTIR to investigate the chemical bonding of the composite membrane. Observations were done on the percentage of emission against wave numbers in regions of certain wave number. Spectral peaks depic the type of chemical bonds existing in the sample (Ruichun Jiang et al., 2006; Ramani et al., 2005).

Infrared spectra obtained at the wavelength of (400 to 4000) cm-1 are shown in Figure 4.7 (a to d) in Mahreni, 2009. Such images show that spectral peaks of the composite membrane shift when the content of inorganic component changes. In this figure show the chemical

reaction between a group of sulfonic-SiO₂ and SiO₂-PWA as indicated by the peak shift in the infrared spectrum of pure Nafion membrane and composite membranes does occur. Vibration of COC bond on NS10W at wave number of 969 cm⁻¹ shifts to lower wave number. Wave number shift may mean that it had been occurred interaction between the sulfonic group and SiOH. The interaction is stronger when the higher content of SiOH (Ramani et al., 2004; Shao et al., 2003; Je-Deok Kim & Itaru Honma 2004). Clear explanation in detail have been presented in the previous publication in (Mahreni et al., 2009).

6.7 TEM analysis

Fig. 12 (a) to (c) show the cross sectional of NS10W, NS15W and NS20W composite membrane with 60 000 X magnification using TEM.



Fig. 11. Cross sectional composite membrane (a) NS10W, (b) NS15W and (c) NS20W with 60,000 X magnification using TEM (Mahreni et al, 2009).

Fig. 11 shows the size of inorganic particles (Si and PWA) in the NS10W, NS15W and NS20W composite membranes, respectively, are 6,9 nm, 7,864 nm and 12,641 nm. Distribution of particles is found there are more in the NS20W membrane than in the NS 10 and NS15W membranes. NS20W membrane particle size found to be larger than the NS10W and NS15W membranes which caused by the agglomeration of particles causes the inorganic particles are in the space of the polymers. SiO₂ and the PWA particle sizes in the NS10W and NS15W composite membranes smaller than cluster size of Nafion causes the both particles trapped in the Nafion cluster and make the conductivity of Nafion increases compared to NS20W membrane having a larger particle size than Nafion cluster size. XRD analysis also shows the location of SiO₂ and PWA particles contained in the composite membrane.

7. Application of the composite membran as electrolyte in the PEMFC

The composite membrane NS10W, NS15W, NS20W and N112 (pure Nafion), was applied as electrolyte in PEMFC.

7.1 Membrane electrode assemblies (MEA)

The membrane was sandwiched between the two electrodes (GDE) and then hot pressed at 130°C and 70 atm for 90 s to obtain membrane electrode assembly (MEA). Single cell of PEMFC consist of the current collector, bipolar plat in both side of MEA. External circuit is equipped to join anode side and cathode side. Flow chart of the membrane application in the PEMFC is depicted by Fig. 12.



Fig. 12. Flowchart singgle cell test of Nafion-SiO₂-PWA membrane as electrolyte of PEMFC.

7.2 Analysis of the electrochemical properties of composite membranes using FCTS (Fuel cell test system)

Electrochemical analysis is carried out in order to determine the performance of the composite membranes when it used as electrolytes in PEMFC. To determine the electrochemical properties of the membrane, the membrane is combined with gas diffusion layer (GDL) and catalyst layer (anode and cathode) with a hot pressing method at specified temperature and pressure to produce membrane electrode assemblies (MEA) (Frey & Linardi, 2004). The single cell of PEMFC is fabricated with sandwich MEA with bipolar plates, the current collector and an external circuit that connect anode and cathode. Single cell is then tested by using fuel cell test station (FCTS). Single cell test is performed to obtain data that represent the performance of the composite membrane as electrolyte at certain operating conditions. The FCTS is equipped with a sensor and controllers of hydrogen fuel and oxygen rate, temperature and pressure.

8. Conclussion

The Nafion-SiO₂-PWA composite membrane has been produced via sol-gel technique solution phase. The result from the characterization, it can be seen that the composite membrane has the properties of water absorption which is higher than pure Nafion membrane. Thermal resistance property of the composite membrane is higher than the Nafion membrane. The structure of all of composite membranes is homogeneous its diameter is in nanometer level. Results of X-ray observation shows that SiO₂-PWA particles are inside the cluster of NS10W, NS15W composite membranes, but the particle location is outside of Nafion cluster in the NS20W membrane. Results of FTIR and X-ray energy dispersion observation showing that the silica and tungstic components are bound to the matrix of Nafion polymer prove that the silica and tungstic components added to the Nafion membrane are not be separated from the matrix of Nafion polymer chains. The particles diameter of the composite Nafion-SiO₂-PWA membranes in the range of 7 up to 13 nm.

Data obtained from FCTS for each type of membrane used as electrolyte in PEMFC are voltage and current density that can be recorded. Membrane performance was analyzed indirectly by analyzing the (V-I) data for each membrane. Every different type of membrane, resulting different (V-I) curve. Therefore, each data reflects the membrane performance when operating parameters such as hydrogen and oxygen rate, temperature, pressure, and other parameters are constant. Analysis with fuel cell test station showed that higher current density was produced by nanocomposite membrane (82 mAcm⁻² at 0.6V for NS15W) than with the Nafion membrane (30 mAcm⁻² at 0.2 V) at 90 °C and 40% relative humidity.

9. References

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Synthesis, Surface Modification and Characterisation of Nanoparticles

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1. Introduction

Nanoparticles with sizes ranging between objects and microparticles (e.g. atom) have attracted much attention. These particles with various specialized functions not only deepen our understanding of nature, but also serve as the basis for the development of new advanced technology.

The successful application of nanoparticles depends upon both the synthesis and the surface modification of these particles. Surface modification can improve the inherent characteristics of the nanoparticles and serve to prepare nanocomposites inexistent in nature.

Nanocomposites are made from two or more of the solid phase, at least in one dimensional nano-level size (1-100 nm). The solid phase can be amorphous, semi-crystalline, grain, or a combination. The solid phase can also be organic, inorganic, or a combination. According to the size of the solid phase, nanocomposites generally include the following three types: nanoparticles and nanoparticle compounds (0-0 composite), nanoparticles and conventional bulk composites (0-3 composite) and composite nano-films (0-2 composite). In addition, the nano-layered structure material is ascribed to nano-material, and the multi-layer nanocomposite composite composites is also known as nanocomposites.

Composite materials own excellent performance, which can be widely used in aerospace, defense, transportation, sports and other fields. Nanocomposites are one of the most attractive part of the composite materials. Due to the fast development in recent years, nanocomposites are put in an important position by the developed countries in the development of new materials. The research on nanocomposites includes organic-inorganic composites, nano-polymer matrix composites and inorganic-inorganic composites. In this chapter, combined with our research experience, we mainly introduce the nano-polymer matrix composites to the readers. In order to claim the nano-polymer matrix composites exactly, synthesis and modification of nanoparticles and preparation, characterization and applications of nano-polymer matrix composites were mainly discussed.

2. Synthesis and modification of nanoparticles

2.1 Synthesis of nanoparticles

Nanoparticles are solids particles at the intermediate state, that is between atoms/molecules and macroscopic objects. Owning small size effect, large surface effect and quantum tunnel effect, the nanoparticles demonstrate special physical properties and can be widely used in high density magnetic recording, radar signal absorbing, magnetic fluid, radio wave shielding, precision polishing, optical devices, thermal conducting gel for micro chips, electronic packaging, optoelectronics, high-performance battery, solar cell, efficient catalyst, efficient fire retardant, sensitive components, high-toughness ceramics, the body repairing, cancer therapy, and so on. Preparation of nanoparticles is an important branch of the materials science and engineering. The study of nanoparticles relates various scientific fields, e.g., chemistry, physics, optics, electronics, magnetism and mechanism of materials. Some nanoparticles have already reached practical stage. In order to meet the nanotechnology and nano-materials development in the next century, it is necessary to review the preparation techniques of nanoparticles.

Methods for preparation of nanoparticles can be divided into physical and chemical methods based on whether there exist chemical reactions. On the other hand, these methods can be classified into gas phase, liquid phase and solid phase methods based on the state of the reaction system. The gas phase method includes gas-phase evaporation method (resistance heating, high frequency induction heating, plasma heating, electron beam heating, laser heating, electric heating evaporation method, vacuum deposition on the surface of flowing oil and exploding wire method), chemical vapor reaction (heating heat pipe gas reaction, laser induced chemical vapor reaction, plasma enhanced chemical vapor reaction), chemical vapor condensation and sputtering method. Liquid phase method for synthesizing nanoparticles mainly includes precipitation, hydrolysis, spray, solvent thermal method (high temperature and high pressure), solvent evaporation pyrolysis, oxidation reduction (room pressure), emulsion, radiation chemical synthesis and sol-gel processing. Solid phase method includes thermal decomposition, solid state reaction, spark discharge, stripping and milling method.

We have synthesized several nanoparticles in our laboratory, such as: TiO₂, Fe₃O₄, ZnO, SiO₂ and YIG nanoparticles.

2.1.1 Synthesis of titania nanoparticles

Using titanium tetrachloride (TiCl₄) as a precursor [1], titania nanoparticles were synthesized in the diffusion flame (DF) of air and liquid petrol gas (LPG). The effects of air and LPG flow rates and flow ratio, flame temperature and flame shape on the synthesized TiO₂ nanoparticles were investigated. Experimental investigation, performed using the apparatus in Fig. 1, showed that the mean particle size of TiO₂ increased obviously with



Fig. 1. Experimental flow diagram for synthesizing TiO₂ nanoparticles using LPG/air flame. (1 and 1': Dryer, 2: TiCl₄ evaporator, 3 and 3': rotameters, 4: thermometer, 5: combustor, 6: filter, 7: circulating-water vacuum pump, 8: air compressor, 9: LPG cylinder) [1].

increasing airflow rate, and not obviously with that of LPG, the mean particle size at optimal experimental condition was less than 20 nm, the rutile fraction in the synthesized powder increased with increasing flame temperature and the particle size was affected by the flame height. A particle-dynamic model, describing the nucleation and coagulation of titania monomers/nanoparticles, was used to account for the experimental results based on the isothermal assumption. Generally speaking, the calculated particle sizes from the particle dynamics were consistent with the experimental measurements, especially, when the feed concentration of TiCl₄ was low.

2.1.2 Microwave synthesis of magnetic Fe₃O₄ nanoparticles

Magnetice (Fe₃O₄) nanoparticles were prepared by the co-precipitation of Fe³⁺ and Fe²⁺, NH₃ H₂O [2] was used as the precipitating agent to adjust the pH of the suspension, and the aging of Fe₃O₄ magnetic nanoparticles was accelerated by microwave (MW) irradiation [3]. The obtained Fe₃O₄ magnetic nanoparticles were characterized by Fourier-transform infrared spectroscopy (FT-IR), transmission electron microscopy (TEM), X-ray diffraction (XRD) and vibrating sample magnetometer (VSM).

The average size of Fe₃O₄ crystallites was found to be around 8-9 nm. Aged under MW irradiation, Fe₃O₄ nanoparticles have more complete crystalline structure than those aged for 7 days at room temperature. The obtained nanoparticles are well indexed to the inverse cubic spinel phase of Fe₃O₄. In addition, it can be seen from Fig. 2 that Fe₃O₄ nanoparticles aged under MW irradiation have a higher saturation magnetization than those aged for 7 days at room temperature, which is due to the well crystallinity of Fe₃O₄ nanoparticles. Compared to Fe₃O₄ nanoparticles aged for 7 days, the coercivity of samples aged under MW irradiation increased, which could be ascribed to the reduction of particle size of Fe₃O₄.



Fig. 2. Magnetic hysteresis curves of Fe₃O₄ nanoparticles (sample A was aged under MW irradiation (a) and sample B was aged for 7 days at room temperature (b), respectively) [2].

2.1.3 Magnetic field synthesis of Fe₃O₄ nanoparticles

Fe₃O₄ nanoparticles were prepared by co-precipitation, and the aging of nanoparticles was improved by an applied magnetic field [4]. The obtained nanoparticles were characterized by FT-IR, scanning electron microscopy (SEM), XRD, and VSM. The results show that synthesized under an applied magnetic field, the aging time could be greatly reduced and the magnetic properties of Fe₃O₄ nanoparticles could be improved.

2.1.4 Synthesis of Fe₃O₄ nanoparticles without inert gas protection

 Fe_3O_4 nanoparticles were hydrothermally synthesized under continuous MW irradiation from FeCl₃ 6H₂O and FeSO₄ 7H₂O aqueous solutions, using NH₄OH as precipitating reagent and N₂H₄ H₂O as oxidation-resistant reagent [5]. The results of XRD, FT-IR spectroscopy and SEM measurements showed that the synthesized Fe₃O₄ nanoparticles had an average diameter of 10 nm. The magnetic properties of the Fe₃O₄ nanoparticles were measured using a VSM, indicating that the nanoparticles possessed high saturation magnetization at room temperature, as shown in Fig. 3. The Fe₃O₄ nanoparticles synthesized at the optimal ratio of Fe³⁺/Fe²⁺ of about 1.75:1 exhibit a maximal saturation magnetization of 84.83 emu/g. Hydrazine plays double roles both as the precursor of precipitator and as the oxidation-resistant reagent in the reaction system. The saturation magnetization of Fe₃O₄ nanoparticles synthesized with hydrazine was greatly improved.



Fig. 3. (a) Hysteresis regress curve of Fe₃O₄ nanoparticles synthesized using NaOH as precipitator at the ratio (Fe³⁺/Fe²⁺) of 1.75:1 without hydrazine. (b, f, e and d) Hysteresis regress curve of Fe₃O₄ nanoparticles synthesized using NH₄OH as precipitator at the ratio (Fe³⁺/Fe²⁺) of 1.25:1, 1.5:1, 1.75:1 and 2.0:1, respectively, with hydrazine. (c) Hysteresis regress curve of Fe₃O₄ nanoparticles synthesized using NH₄OH as precipitator at the ratio (Fe³⁺/Fe²⁺) of 1.25:1, 1.5:1, 1.75:1 and 2.0:1, respectively, with hydrazine. (c) Hysteresis regress curve of Fe₃O₄ nanoparticles synthesized using NH₄OH as precipitator at the ratio (Fe³⁺/Fe²⁺) of 1.5:1 without hydrazine [5].

2.1.5 Synthesis of ZnO nanoparticles by two different methods

ZnO precursor was synthesized by direct precipitation from zinc acetate and ammonium carbonate [6,7]. ZnO nanoparticles were obtained by calcination of the precursor at 450°C for 3 h and the calcination after the heterogeneous azeotropic distillation of the precursor, respectively. The synthesized ZnO nanoparticles were characterized by FT-IR, XRD and TEM. It is concluded that the heterogeneous azeotropic distillation of the precursor effectively reduced the formation of hard agglomerates, moreover, the photocatalytic activity of the synthesized ZnO nanoparticles is high.

2.1.6 Synthesis of silica powders by pressured carbonation

A method was proposed for the preparation of silica powders using inexpensive material of sodium silicate (Na₂SiO₃) and carbon dioxide (CO₂) by pressured carbonation, in which carbon dioxide acted as a precipitating reagent [8]. The flow sheet diagram is shown in Fig. 4.

Microstructure and size analyses of the precipitated silica powders were carried out using TEM and dynamic light scattering. The average particle size, size distribution and yield of silica powders were affected by reaction time, temperature and concentrations of surfactant and sodium silicate solutions. The particle size of silica powders increased with reaction temperature and concentration of sodium silicate, and the yield of silica powders increased with increasing reaction time, as shown in Table 1. The size distribution of silica powders was affected by concentration of surfactant PEG. The optimal preparation conditions were experimentally determined for obtaining the silica powders with nanometer size, narrow size distribution, spherical shape and high purity without sodium carbonate and surfactant.



Fig. 4. Apparatus for the formation of ultrafine silica powders using carbon dioxide. (R, high-pressure reactor; C, carbon dioxide cylinders; T, temperature controller; I, solution inlet; O, product outlet; G, gas inlet; A, agitator; P1, P2 and P3, pressure gauges; V1, V2 and V3, control values; S, solution injection device) [8].

No.	Temperature	Na ₂ SiO ₃ /mol·L ⁻¹¹	PEG/%	Reaction	Average	Yield/%
	∕°C			time/h	size/nm	
1	80	1.0	5.0	3	54	86.4
2	70	1.0	10	2	52	84.5
3	60	1.0	15	1	46	75.2
4	80	0.50	15	2	36	84.7
5	70	0.50	5.0	1	33	82.3
6	60	0.50	10	3	36	88.6
7	80	0.25	10	1	19	85.3
8	70	0.25	15	3	17	86.3
9	60	0.25	5.0	2	15	86.8

Table 1. Effect of temperature, content of Na₂SiO₃ and PEG, reaction time on the yield and average size of silica [8].

2.1.7 MW-assisted synthesis of Bi-substituted yttrium garnet nanoparticles

Bi-substituted yttrium garnet (Bi-YIG, $Bi_{1.8}Y_{1.2}Fe_5O_{12}$) nanoparticles were prepared by MWassisted co-precipitation as well as conventional co-precipitation using ammonia aqueous solution as precipitant [9, 10]. The nanoparticles were characterized by thermal gravitydifferential thermal analysis, XRD, TEM, dynamic light scattering, VSM and Faraday rotation meter, respectively. Results demonstrate that the Bi-YIG nanoparticles prepared by MW-assisted co-precipitation have smaller particle size, high saturation magnetization (see Fig. 5) and higher Faraday rotation than those prepared by the conventional coprecipitation.



Fig. 5. Magnetic hysteresis of Bi-YIG particles: (M1) prepared by MW co-precipitation and (C2) prepared by conventional co-precipitation [9].

2.1.8 Molten-salt synthesis of Bi-substituted yttrium garnet nanoparticles

Compared to the MW-assisted method [11], Bi-YIG nanoparticles were successfully synthesized by molten-salt method in NaCl-KCl flux at 650°C. XRD, SEM, dynamic light scattering, VSM and Faraday rotation meter were used to characterize the phase, morphology, size distribution, magnetic properties and Faraday rotation of the as-prepared Bi-YIG nanoparticles, respectively. Results show that the average size of Bi-YIG nanoparticles prepared by molten-salt method is about 50 nm. The formation of Bi-YIG in molten-salt process was associated with the type of the raw material used. One can obtain pure Bi-YIG nanoparticles using oxides mixture, but can not obtain pure Bi-YIG nanoparticles using Bi-YIG precursors. The Bi-YIG nanoparticles began to form at 600°C and accomplished at 650°C, and one can obtain pure Bi-YIG phase at the temperature range of 650-800°C using molten-salt method.

2.2 Modification of nanoparticles

To improve or change the dispersion of the nanoparticles, and the compatibility between the nanoparticles and other materials, physical or chemical methods are needed to alter the physical, chemical, mechanical properties, and the surface structure of nanoparticles.

In order to control the surface of nanoparticles and to apply those nanoparticles in industry and biomedicine, in-depth understanding of the basic properties of the nanoparticles are indispensable.

According to the principles of surface modification, the surface modification of nanoparticles can be divided into partial chemical modification, mechanical and chemical modification, external membrane modification (ie, capsule), high-energy surface modification using precipitation, esterification, coupling and grafting reactions. Surface modification in general is through physical adsorption coating or grafting depends on the properties of the particle surface. The use of ultraviolet ray for the plasma surface modification of particles belong to the physical modification. By the chemical reactions between the nanoparticle surface and modifier, the surface structure and state of nanoparticles are changed. Surface chemical modification of nanoparticles plays a very important role to reduce the agglomeration. Due to modifier adsorption or bonding on the particle surface, which reduces the surface force of hydroxyl groups, the hydrogen bonds between particles are eliminated to prevent the formation of oxygen bridge bonds when nanoparticles are drying, thereby preventing the occurrence of agglomeration.

2.2.1 Surface modification of ZnO nanoparticles

ZnO nanoparticles were synthesized by homogeneous precipitation. To reduce the aggregation among ZnO nanoparticles, an effective surface modification method was proposed by grafting polymethyl methacrylate (PMMA) onto the ZnO particles [12]. That is, the surface of ZnO nanoparticles was firstly treated with a KH570 silane coupling agent, which introduces functional double bonds onto the surface of ZnO nanoparticles, followed by radical grafting polymerization in non-aqueous medium. The obtained nanocomposite was characterized by FT-IR, TG, sedimentation test, SEM, and XRD. The results of FT-IR and TG showed that the desired polymer chains have been covalently bonded to the surface of ZnO nanoparticles. It was found that the increasing monomer concentration could increase the grafting percentage and hence promote the dispersibility.

To reduce the aggregation among nanoparticles and to improve the compatibility between nanoparticles and the organic matrix, poly(styrene) (PS) was grafted on to the ZnO nanoparticles in a non-aqueous suspension. The test shows that bare ZnO nanoparticles have high photocatalytic activity, while PS-grafted ZnO composites have almost no photocatalytic activity. Surface modification by grafting polymerization can reduce the aggregation of nanoparticles and help to form a stable suspension in organic solvents.

2.2.2 Surface modification of Fe₃O₄ nanoparticles

In order to prepare stable magnetic fluid, the surface of Fe_3O_4 nanoparticles was modified with different surfactants in our research [13,14].

Using two kinds of surfactants, stable water-based magnetic fluid was prepared. The surface of Fe₃O₄ nanoparticles was coated with oleate sodium as the primary layer and polyethylene glycol 4000 (PEG-4000) as the secondary layer to improve the stability of water-based magnetic fluid [15]. The dosages of oleate sodium and PEG-4000 were found to have an

important effect on increasing the solid content. Gouy magnetic balance showed that the saturation magnetization could be as high as 1.44×10^5 A/m.

To prepare a biocompatible water-based magnetic fluid, the Fe₃O₄ nanoparticles were modified by dextran through a two-step method [16]. The Fe_3O_4 nanoparticles were first surface modified by amino-silane, and then coated by dextran. The influences of dextran molecular weight on the size, morphology, coating efficiency and magnetic property of magnetite/dextran nanocomposite were investigated. The magnetite/dextran nanocomposite was dispersed in water to form a magnetic fluid by ball milling. The molecular weight of dextran plays an important role on the size, morphology, coating efficiency, and magnetic property of magnetite/dextran nanocomposite. The surface modification of Fe₃O₄ nanoparticles with dextran is propitious to the stability of magnetic fluid. The viscosity of magnetic fluid increases with the increasing molecular weight of dextran. An external magnetic field can enhance the interaction among magnetic fluid, therefore, the viscosity of magnetic fluid increases under the external magnetic field. The magnetic field could also rearrange the Fe₃O₄ nanoparticles, leading to the formation of orderly microstructures. When there is no magnetic field, the viscosity of magnetic fluid increases linearly with the solid content. If an external magnetic field is applied, the viscosity increases quadratically with the solid content. Then, the dextran stabilized magnetic fluid were used to perform the MRI experiments on the living rabbits with VX2 malignant tumor, the results showed that these nanoparticles appear to be a promising vehicle for MR imaging [17].



Fig. 6. Synthesis route for the PEG diacid coated magnetite nanoparticles: (1) simplified reaction of hydrolysis and condensation with production of silane polymer; (2) scheme of the simplified silanization reaction of APTES on the magnetite surface; (3) simplified reaction of HOOC-PEG-COOH on the magnetite surface after treated by APTES [17].



Fig. 7. T2-weighted MR images acquired before (a) and at different times after the injection of magnetic fluid (b: 30 min, c: 60 min, d: 90 min, e: 120 min) [17].

In addition, we prepared kerosene-based magnetic fluid via a simple one step phase-transfer method [18]. The Fe₃O₄ nanoparticles formed in the aqueous phase firstly modified by oleic acid and then migrated to the organic phase of kerosene to form a magnetic fluid. The size of Fe₃O₄ nanoparticles was found to be around 10 nm by TEM. The magnetic fluid demonstrated superior stability, and had susceptibility of 7.78×10^4 and saturation magnetization of 27.3 emu/g. The rheological property [19] of the prepared magnetic fluid was investigated using a rotating rheometer attached with a custom-built solenoid coil. It was found that the viscosity of the magnetic fluid increased with the increasing intensity of magnetic field, and the magnetic fluid demonstrated shear-thinning behavior and could be described by the Herschel-Bulkey model.



Fig. 8. A rotating rheometer for measuring viscosity under applied magnetic field [18].

2.2.3 Surface modification of silica nanoparticles

To prepare excellent silica reinforced PMMA [14,20], we first modified the silica with silane coupling agent (g-methacryloxypropyl trimethoxy silane, KH570), followed by in situ bulk polymerization. The modified silica nanoparticles were characterized by FT-IR, TEM and TG. Sedimentation tests and lipophilic degree (LD) measurements were also performed to observe the compatibility between the modified silica nanoparticles and organic solvents. The resultant polymers were characterized by UV-vis, Sclerometer, differential scanning calorimetry (DSC). The mechanical properties of the hybrid materials were measured. The results showed that the glass transition temperature, surface hardness, flexural strength as well as impact strength of the silica-nanoparticle reinforced PMMA slices were improved. Moreover, the tensile properties of PMMA films doped with silica nanoparticles via solution blending were enhanced.



Fig. 9. Effects of silica nanoparticles on the properties of PMMA films. 1: neat PMMA, 2: unmodified silica+PMMA, 3: KH570-grafted silica+PMMA, 4: PMMA-grafted silica+PMMA [20].

3. Preparation and characterization of polymer-inorganic nanocomposites

3.1 Nano-polymer matrix composites

Since the sixties of the 20th century, P.J. Flory began to study the chain structure of polymer in solution. He thought that the polymer structure can be divided into three levels. One is chain structure, such as polyethylene; the second is conformation structure, such as isotactic polypropylene and syndiotactic polypropylene; the last is condensed state, such as liquid crystal polycarbonate, semi-crystalline polyether ether ketone, and so on. After different researches, researchers have proposed several models for the polymers possessing secondary or tertiary structure, as shown in Fig. 10.

Polymer possessed condensed state mainly refers to crystalline state, and the crystalline spherulites form is shown in Fig. 11. The condensed state can be divided into four phases, namely: no fixed shape, the transition state, liquid crystal state and crystalline state. Ascribing to the complex formation process and peculiar phenomenon, transition state and liquid crystal state have attracted much attention. The crystalline state is interesting mainly due to its multi-crystalline form.

Secondary structure↔



Fig. 10. Several models for the polymers possessing secondary or tertiary structure.



Fig. 11. Crystalline spherulites form of polypropylene under polarizing microscope [21]

Nano-composite material is the combination of the nano-sized powders and the the polymer matrix. In such materials, organic polymer generally is a continuous phase, and the nanoparticles the dispersed phase, such as, Bil₃-nylon11 nanocomposites and nylon-montmorillonite nanocomposites. In the new century, the rapid development of nano-composite materials becomes one of the most advanced composite materials.

When the nanoparticles were introduced into organic polymer matrix, the polymorphic crystalline would be induced, giving the nano-polymer matrix composites many excellent properties. Advantages of the nano-polymer matrix composites mainly include: (1) the increased properties of polymers, such as higher heat distortion temperature, rapid crystallization, improved mechanical properties, etc.; (2) a resource-saving compound, using only the common raw materials, and no other new materials; (3) the original process route: nano-composite uses the original route of polymer processing. These features make the nanocomposites easier to produce industrially, once breakthrough was obtained. In other words, nano-polymer matrix composites can provide an epoch-making performance by adjusting the complex dispersion of the original materials.

Polymer-inorganic nanocomposites own the machinability of organic materials and the functional and structural properties of inorganic materials, becoming the hot spot of today's science and technology. In the nanocomposites, a large part of the nano-materials is functional. For example, Bil₃/nylon11 nanocomposites show X-ray induced conductivity, the nanoparticles in the PS-clay nanocomposites display liquid crystal inducing behavior, and a-FeOOH is used as a nuclear assembly agent in polymer LB films, and so on. In addition, nanomaterials provide directional characteristics, and its direction-related features, including the coupling characteristics, can be used in the design process. Since the presence of anisotropy and coupling characteristics, the direction and sequence can be designed and tailored, according to the mechanical characteristics and function. With the presence of a dual nature, nano-materials can be more evenly dispersed in the matrix by adjusting the interaction of the interface of the two roles. The intervention of nano-whiskers, nano-rods, nano-wires and nanobeam offers the possibility of the enhanced orientation and maintains the processing facilities of the filled nanoparticles. In the polymer-inorganic nanocomposites, different interfaces also create synergies. To maximize the beneficial effects and synergies of different interfaces of the nanocomposites, the surface modification or treatment is generally appropriated, which forms a link with the substrates (eg covalent, hydrogen bond, intermolecular force, etc.), maximizing the dispersion and the appropriate combination.

Generally, the inorganic materials used to prepare the nano-composites mainly include layered silicate clay, layered compounds, metal powder and a variety of inorganic oxides. In our researches, nano-sized zinc oxide, iron oxide, silica and YIG were synthesized and employed to prepare a variety of polymer nanocomposites, giving the composite materials many new features. The chapter based on our research discusses the methods of preparation and characterization of the polymer-inorganic nanocomposites.

3.2 Preparation of polymer-inorganic nanocomposites

Many methods could be applied to prepare polymer-inorganic nanocomposites, such as solgel processing, in-situ polymerization, particle in-situ formation, blending, radiation synthesis, and so on.

3.2.1 Sol-gel processing

Sol-gel processing is the method that the metal alkoxide or inorganic salt, through solution, sol, gel, curing, and then heat treatment, become solid oxide or other compounds.

Organic/inorganic nanocomposites are usually prepared by sol-gel in the solvent containing precursors and organic polymers. The most direct way is that the precursors hydrolyzed and condensed at the presence of polymer in the solvent systems. If the condition was under control, the polymer would not occur in isolation during the formation and drying process, through which can obtain optical transparent composite materials. Materials prepared by sol-gel processing have uniformity, high purity and low sintering temperature than that by conventional solid state reaction. The biggest problem of sol-gel is that the gel process would lead to a considerable contraction of the internal stress which could result in contraction of brittle materials, due to the evaporation of solvents, small molecules, water. Moreover, this method requires polymers in sol-gel system be dissolved in the condensate. In addition, the precursors are expensive and sometimes toxic, preventing the further improvement and application.

3.2.2 In situ polymerization

This is a class of the simplest and most representative method for the preparation of composite materials. Generally, the inorganic precursor and organic monomer were firstly mixed together, and then water and catalyst were added for condensation of inorganic precursors. Subsequently, oxidant was added for in situ polymerization, and the obtained materials were dried, through which organic/inorganic nanocomposites were prepared. We prepared PMMA/silica nanocomposites by in situ bulk polymerization of a silicic acid sol and MMA mixture [22]. Silicic acid was prepared by hydrolysis and condensation of sodium silicate in the presence of 3.6 M HCl. Silicic acid sol was obtained by tetrahydrofuran (THF) extraction of silicic acid from water. Each set of PMMA/silica composites was subjected to thermal and mechanical studies. With increase in silica content, the PMMA/silica nanocomposites filled with silica particles showed improved thermal and mechanical properties, whereas a decrease in thermal stability.

3.2.3 Particle in situ formation

Polymers and inorganic hybrid precursors were dissolved in a suitable solvent, and the molecules of polymer and precursors combined together. Via a reaction, such as metal alkoxide hydrolysis, oxidation and reduction reactions, and so on, inorganic nanoparticles were in-situ formed in the polymer. Using the adsorption and complexation of metal ions of polymer-specific functional groups or the space constraints between polymer and reactant, nanocomposites were prepared in situ. The methods for generating nanoparticles can be radiation, heat, light, gas reactions, and so on. By this way, the obtained inorganic particle was usually nanometer size, and uniformly dispersed in polymer. Therefore, the compounds own a transparent stable structure. Moreover, the polymer plays a role of size controlling and aggregation preventing of inorganic nanoparticles. In our research, ultrasmall magnetite nanoparticles were prepared using chitosan-polyacrylic acid (CS-PAA) nanospheres as template [23]. The CS-PAA hollow nanospheres could be prepared by polymerization of acrylic acid monomers in the presence of chitosan. The Fe₃O₄ loading was done by dissolving FeCl₃ 6H₂O and FeSO₄ 7H₂O into CS-PAA nanospheres solution followed by adding NH₄OH. Finally, CS-PAA template could be removed by adjusting with HCl to pH < 1. The obtained particles were characterized by dynamic light scattering (DLS) in aqueous solution and observed by TEM, FT-IR and X-ray. The results revealed that the Fe₃O₄ nanoparticles were 3-5 nm in size with excellent dispersibility. The particles exhibited superparamagnetic property with saturation magnetizations of 40.7 emu/g.



Fig. 12. The procedure for monodisperse magnetite nanoparticles via chitosan-poly(acrylic acid) template [23].



Fig. 13. TEM images of (a) bare Fe₃O₄ nanoparticles; (b) CS-PAA particles; (c) magnified CS-PAA particles; (d) Fe₃O₄ nanoparticles synthesized by CS-PAA template [23].

3.2.4 Blending

Blending is the simplest way to prepare nanocomposites, and is suitable for all kinds of nanoparticles. According to the conditions, blending usually can be divided to solution blending, emulsion or suspension blending and melt blending.

3.2.4.1 Solution blending

Firstly, the nanoparticles were added after the base resin was dissolved in solvent. The obtained mixture was agitated to prepare a uniform mixture. The nanocomposites were prepared by removing the solvent or making polymerization of the monomer. In our research, polyurethane- based coatings reinforced by ZnO nanoparticles (about 27 nm) were prepared via solution blending [24]. The ZnO/PU films and coats were fabricated by a simple method of solution casting and evaporation. The mechanical properties of the films were investigated by a universal material test, and the abrasion resistance of the prepared coats was evaluated by a pencil-abrasion-resistance tester. It was found that significant improvement of the PU films in Young's modulus and tensile strength was achieved by incorporating ZnO nanoparticles up to 2.0 wt%, and that the abrasion resistance of the PU coats was greatly enhanced due to the addition of ZnO nanoparticles. Moreover, the antibacterial property test was carried out via the agar dilution method and the result indicated that PU films doped with ZnO nanoparticles showed excellent antibacterial activity, especially for *Escherichia coli*.



Fig. 14. Tensile stress-strain curves of different PU films [24].

ZnO(wt%)	Antibacterial rate	Antibacterial rate		
	Escherichia(CPU)	Bacillus subtillis(CPU)		
0	0	0		
1.0	20	0		
2.0	26	18		
3.0	71	61		
4.0	90	84		

Table 2. Antibacterial rate of PU films containing different content of ZnO nanoparticles [24].

Besides, the Bi_xY_3 -xFe₅O₁₂ (x = 0, 1 and 1.8)-doped PMMA nanocomposites were prepared by in situ bulk polymerization [25]. Some $Bi_xY_3-xFe_5O_{12}$ nanoparticles (0.05 wt%) were dispersed in MMA monomer, and the obtained suspension was mixed in a highperformance ball mill operating at 40 rpm for 4 h. Some AIBN (0.1 wt% of monomer) as initiator was added. The prepolymerization was performed at 80 ± 2°C under mechanical stirring for about 20 min until the conversion of MMA was about 12-15%. Then, the suspension was poured into a stainless steel mold, which was coated with a thin film of Garry Mould Release Agent (non-paintable). The aperture at the top of the mold was wrapped with a plastic foil. Thereafter, the mold containing the prepolymer and $Bi_x Y_3$ - $_{x}$ Fe₅O₁₂ nanoparticles was kept at 40°C for 24 h, and the solidification took place. Then, the temperature was adjusted to 100°C and kept for 1 h to increase the molecular weight of PMMA. Finally, $Bi_x Y_{3-x} Fe_5 O_{12}$ (x = 0, 1 and 1.8)-doped PMMA nanocomposites were obtained after disassembling the molds. The PMMA slice doped with Bi-YIG nanoparticles is a new promising material for magneto-optical devices. The Faraday rotation test showed that the angle of Faraday rotation increased with increasing Bi content in PMMA composites, and the maximum figure of merit was 1.46°, which was comparable to the value of a sputtered film.

3.2.4.2 Emulsion or suspension blending

Similar to solution blending, emulsion or suspension solution was used instead of solution [26]. The method is mainly applicable to the case of polymer difficult to dissolve. Superparamagnetic magnetite/polystyrene composite particles were prepared by inverse emulsion polymerization with water-based magnetic fluid as dispersing phase and organic solvent and styrene as continuous phase. The resultant brownish Fe₃O₄/PS emulsion showed magnetism in an applied magnetic field. The obtained magnetic Fe₃O₄/PS microspheres were characterized by FT-IR, TEM, SEM, XRD and TG. The magnetic Fe₃O₄/PS microspheres with a diameter of 200 nm were observed. The results showed that magnetite particles were well encapsulated in PS and the composite particles have high magnetite contents, which was more than 15%.



Fig. 15. The procedure for preparation of Fe_3O_4/PS composite particles by inverse emulsion polymerization (left); TEM images of Fe_3O_4/PS composite micropheres (right) [26].

3.2.4.3 Melt blending

To prevent aggregation, the surface of the nanoparticles was firstly modified with a suitable agent, and then the nanoparticles were added to the polymer in the molten state uniformly. Advantage of the method is similar to ordinary polymer modification, and is easy to industrialization. LDPE/EGP electrical conducting composites were prepared using low density polyethylene (LDPE) and expanded graphite (EGP) via melt blending [27]. The effects of EGP on the electrical and mechanical properties and Positive Temperature Coefficient (PTC) of the prepared composites were investigated. Results showed that the tensile strength of the composites decreased with the increasing content of EGP, and the EGP content should be lower than 40%. The PTC strength of the composites increases firstly and then decreases along with the increasing EGP content and achieved the maximum value of about 5.85 at 33% of filling content. Moreover, it was found that the PTC strength of the composites was affected by the heat treatment and blending time.



Fig. 16. SEM of the fracture of EGP/LEDP composites (35% EGP, no phase separation) [27].

3.2.4.4 Mechanical grinding blending

Using mechanical grinding blending, many kinds of magnetic fluids could be prepared. Firstly, polymer and some surfactants were resolved in a solvent. Then, some magnetic nanoparticles were added and mixed together. The mixture was ball milled at 40 rpm for 3 h at room temperature using a high-performance ball mill under airtight condition. The pots and balls were made of agate. After ball milling for a suitable time, magnetic fluids were prepared.

3.2.5 Others

Recently, there are many reports on the use of special methods for preparing polymer/inorganic nanocomposites, such as MD and LB membrane method and radiation synthesis. In the LB membrane method, single or multilayer film is firstly pre-formed with metal ions, and then reacted to form sulfide nanoparticles. MD membrane method is the

way, using electrostatic interaction between cation and anion, to prepare single or multiordered membrane. Radiation synthesis is a recently developed method for the preparation of nanocomposites. Firstly, polymer monomer and metal salt mixed together at the molecular level, and then reacted under irradiation. The preparation method according to the system can be divided into two ways: the water system and the non-water system.

3.3 Characterization of polymer-inorganic nanocomposites

As we all know nanomaterials possess the following characters: small size and large specific surface area, high surface energy, a large proportion of surface atoms. As a result, one must have special "eye" and "hand" to characterize the nano-scale structure and properties of materials, and to effectively control its size, morphology, crystalline phase, composition and structure.

3.3.1 X-ray diffraction

From the XRD data, one can obtain the material composition, structure (three-dimensional coordinates of atoms, chemical bonding, molecular conformation and three-dimensional conformation, the electron density value, etc.) and the information on the interaction between molecules. XRD is a common means of measuring nanoparticles. It can not only determine the sample phase and the phase content, but also the particle size. When the grain size is less than 100 nm, the diffraction line broadening will occur. The diffraction lines of the half-peak width of degree β department and crystal grain size (D) has the following relationship:

$$\beta = 0.89\lambda / D\cos\theta$$

Accordingly, the strongest diffraction peak can be used to calculate the particle size of the prepared nanomaterials.

From X-ray photoelectron spectroscopy one can obtain the following information: (1) the element contents, except H and He from the fingerprint of the Eb (the binding energy of atoms in a particular orbit) spectrum. (2) the chemical valence state, chemical structure and physical state according to displacement of peak and the shape. (3) the semi-quantitative element analysis of chemical states from the relative intensity ratio of peak. (4) different elements, chemical state depth distribution and the film thickness from the peak and the change of the background intensity. In general, the higher Eb, the less electron density corresponding to the element is.

In our research, it was found that the magnetism of Fe_3O_4 nanoparticles vanished at 550°C when exposed in the atmosphere for 2 h [28]. To find the reason of magnetism vanishment of pure Fe_3O_4 nanoparticles, XRD was performed using Cu Ka radiation. The XRD patterns of pure Fe_3O_4 nanoparticles calcined at different temperatures are shown in Fig. 17. One can find from the that there is almost no difference among the diffraction peaks of the particles calcined at 150°C and 250°C except the weakening in intensity of magnetite, especially for (3 1 1) peak. From 350°C to 550°C, the (3 1 1) peak keeps reduction, while (1 0 4) peak of hematite develops and becomes increasingly stronger. The magnetite (Fe_3O_4) transforms to hematite (*a*-Fe₂O₃) completely at 550°C, and the the magnetism of the nanoparticles vanished.



Fig. 17. XRD patterns of pure Fe_3O_4 nanoparticles at room temperature (a) and calcined at 150°C (b), 250°C (c), 350°C (d), 450°C (e), 550°C (f) for 2 h in the atmosphere [28].

3.3.2 Infrared spectroscopy (IR)

From the IR spectrum, one can observe the absorption and emission due to the molecular vibration and rotation in the electromagnetic wave infrared region (15000~10 cm⁻¹). It reveals the unknown composition qualitatively according to the bands characteristic frequency, determines a component content of the sample (quantification) according to band intensity. It can also reveal the molecular structure (such as functional group, bond), identify isomer, and determine structures of compounds. The interaction among molecules can also be understood by anatomizing the band change. This method can be used to measure samples in the state of gas, liquid and solid. There are also extremely sensitive changes in molecular structure called "fingerprint zone" (1300~400 cm⁻¹), which provides a reliable determination to analyze unknown composition and structure.

Figure 3-8 shows that no change of XRD patterns can be observed for pure Fe_3O_4 nanoparticles after being calcined at 150°C and 250°C. To reveal the difference, IR spectra (as shown in Fig. 18.) of magnetite samples calcined at different temperatures were obtained using FT-IR. From Fig. 18., one can find the absorption peak of Fe-O in Fe₃O₄ at 571.1 cm⁻¹. After calcined at 150°C for 2 h, the peak at 571.1 cm⁻¹ splits into two peaks at 632.9 and 563.4 cm⁻¹, respectively. The new arisen absorption peaks at 632.9 and 563.4cm⁻¹ which are associated with Fe-O bond, are the characteristic peaks of γ -Fe₂O₃. XRD is not sensitive enough to differentiate between Fe₃O₄ and γ -Fe₂O₃, due to extreme similar similarity in crystal structure of the two phases. Provided that there is an intergradation, in which Fe₃O₄ and γ -Fe₂O₃ coexist at a certain proportion that owns the maximal magnetism. The intergradation appears when the pure Fe_3O_4 nanoparticles were calcined at 250°C for 2 h in air, leading to the maximal magnetism. Afterwards, the peak at 632.9 cm⁻¹ becomes increasingly weaker, and disappears at 550°C. While, another new peak at 447.6 cm⁻¹ comes forth at 450°C, and the peak becomes stronger and shifts to 463.1 cm⁻¹ when at 550°C. According to Nasrazadani and Raman the two absorption peaks at 532.5 cm⁻¹ and 463.1 cm⁻¹ can be assigned to the Fe-O absorption in hematite (a-Fe₂O₃). Therefore, one can get that 550°C is the minimal temperature for the complete transformation from magnetite (Fe_3O_4) to hematite (a-Fe₂O₃), consistent with the results of XRD and magnetic properties analysis.



Fig. 18. IR spectra of pure Fe_3O_4 nanoparticles at room temperature (a) and calcined at 150°C (b), 250°C (c), 350°C (d), 450°C (e), 550°C (f) for 2 h in the atmosphere [28].

3.3.3 Mechanical property test

The mechanical property of the prepared films can be measured using the universal material testing machine (WDT-0.2, KQL Testing Instruments Inc., China). The force transducer with a precision of $\pm 0.02\%$ was made by Transcell Tech. Inc., USA. The maximum range of the transducer is 30 kg. The crosshead speed was 5 mm/min during the tests. The films were cut into dumb-bell shape and the mechanical property measurement was performed according to our previous articles.

The mechanical property of pure PU films and ZnO-doped PU films prepared using PU coatings were measured [29]. Fig. 14. shows the tensile stress-strain curves of the PU films and the mechanical parameters are listed in Table 3. It can be seen that the Young's modulus and tensile strength increase first and then decrease with the increasing ZnO content and the optimal ZnO content for the Young's modulus and tensile strength is obtained at 2.0 wt%. However, the elongation at rupture goes inversely relating to the Young's modulus and tensile strength. Repeated tests show that the filled ZnO nanoparticles can enhance the strength but not the flexibility of the composite films. The elevation of Young's modulus and tensile strength of the composite films may be due to the limit of moving scale of chain segments of the PU matrix with the addition of ZnO. Moreover, when ZnO nanoparticles are filled into the interstice of PU chains, an interactive force against the PU chains may be generated. Therefore, when an external force is applied onto the two ends of the dumb-bellshaped PU film, the film goes to rupture easily due to the strong interaction force generated between ZnO nanoparticles and PU chains. Besides, the percolation effect could cause the aggregation of ZnO nanoparticles in the dry film, leading to the deterioration of mechanical property.

ZnO (wt%)	Young's modulus	Tensile strength	Elongation ratio
	(MPa)	(MPa)	At rupture (%)
0.0	517.42	8.58	98.37
1.0	660.34	16.74	94.35
2.0	710.48	17.83	54.79
3.0	557.70	10.42	77.96
4.0	512.76	7.24	70.69

Table 3. Mechanical property of the PU films filled with different ZnO content [29].

3.3.4 Abrasion resistance test

The neat PU coatings and 2.0 wt% ZnO nanoparticles filled PU coatings were sprayed onto a ABS substrate with a 1 mm×1 mm grounding area. The obtained wet coat was roasted for curing under infrared ray at 60°C for 30 min. The abrasion resistance of the selected coat was tested using a pencil-abrasion-resistance tester. In the testing process, a sample area, which was free of blemishes and painting imperfection, was selected. The eraser was kept closely contacting with the surface of the sample at 90°. The moving distance was limited to 2.54 cm, and the frequency was maintained at 25 rpm. The test was performed by moving the free end of the pencil until the grounding area, which was a useful indicator when some cracks were made, was revealed. The total times of the eraser moving back and forth indicate the abrasion resistance of the coat.

Table 4. shows the abrasion resistance of the dry and alcohol wetted PU composite coats. It demonstrates that the abrasion resistance of the composite coats is improved when ZnO nanoparticles were filled into the PU matrix. The improvement of abrasion resistance for the samples with ZnO nanoparticles may be attributed to the polymer bond formed around the hard nanoparticles. Compared with the dry coats, the wet coats demonstrate poor abrasion resistance, indicating poor endurance against organic solvent, such as alcohol. Besides, one can also see that the abrasion resistance of the dry and wet coats is linear to the thickness, and the slopes are 0.9664 (dry, neat), 0.9906 (wet, neat), 0.9910 (dry, composite) and 0.9937 (wet, composite), respectively. Moreover, the PU composite coats possessing the same abrasion resistance are much thinner than the pure PU coats, which revealing that the addition of ZnO nanoparticles, is favorable for reducing manufacturing cost and displays an outstanding prospect in application.

Thickness	Neat PU film		Compo	osite film (2.0 wt% ZnO)
(µm)	Dry	Wetted with alcohol	Dry	Wetted with alcohol
10	148	60	361	86
12	155	77	410	97
14	162	91	437	113
16	187	101	497	133
18	206	110	560	156

Table 4. The abrasion resistance of the composite coats with various thickness from 10 to 18 μ m [23].

3.3.5 Impact strength

To obtain the impact strength of nanocomposites, an Izod impact machine tester with digital display (JBL-22, Shenzhen KQL Testing Instruments Co., Ltd) was used according to GB/T 1843-1996. Unnotched specimens with rectangular dimensions of $80 \times 10 \times 4$ mm³ were fractured by the impact energy of 5.5 J with an impact speed of 3.5 m/s at room temperature. The distance between the impact point and fixed point was set to 22 mm.

The impact strength of PMMA nanocomposites is shown in Fig. 19. For Sample A, the filling of silica particles obviously improves the impact strength of PMMA nanocomposites. The impact strength of PMMA nanocomposites increases with the increasing silica content, which can be ascribed to the more reinforcement sites formed among the polymer chains. It suggests the importance of incorporating the silica particles to improve the mechanical properties of PMMA nanocomposites. Considering the strong increase in impact strength of PMMA nanocomposites, it is obvious that some energy is eliminated by the filled silica particles during the breaking-down process. As for Sample B, the impact strength is enhanced at low content of silica (x = 0.5) and then weakened at high content (x = 1 or 1.5). With the increasing silica content, more THF is left in the polymer composites and thereafter induces the formation of small pin-holes in PMMA during the heat treatment at 100°C. During the test of impact strength, such pin-holes become the weak points and the PMMA nanocomposites are easy to be broken under an abrupt impact and the impact strength decreases.



Fig. 19. Impact strength of different PMMA nanocomposites [14].

3.3.6 Flexural test

Flexural test could be performed according to GB/T 9341-2000²⁶ using a universal testing machine (WDT20, Shenzhen KQL Testing Instruments Co., Ltd) in a three-point bending configuration at room temperature. A PC was connected to the testing machine, and the crosshead speed was set to be 2 mm/min. Another force transducer with a maximum range of 2 ton is used. The transducer with a precision of $\pm 0.02\%$ was made by Transcell Tech. Inc. USA. The effect of particulate fillers on the stress-strain behavior of polymeric materials can be much different due to the interaction between the particles and polymer. The flexural
strength measured for different PMMA nanocomposites is shown in Fig. 20. It can be concluded that as the silica content increases, the flexural strength of PMMA nanocomposites either filled by silica particles or by silicic acid sol increases. The reinforcement mechanism of polymer by silica can be explained as this: as the active surface of silica particles connected with some long polymer chains and the physical bonding between silica and polymer chains are formed, the flexural stress could be transferred through the inorganic linking point to the other polymer chains. When one chain gets ruptured under external stresses, the others can still support the polymer structure. So the whole specimen is not threatened by the stresses, and the flexural strength enhances. For the Sample A, as the content of silica particles increased, the number of coupling points between PMMA and silica particles also increased; therefore, the flexural strength is improved. As for Sample B, contrary to the impact strength, the flexural strength is enhanced with the addition of more silicic acid sol, though there maybe small pin-holes existing in the composites. There are two factors influencing the flexural strength of PMMA nanocomposites: the addition of silica and the existence of pin-holes in the structure. During the test, stress was imposed slowly on the samples, though the pin-holes might lower the flexural strength; however, such influence was negligible. On the contrary, the silica well dispersed in PMMA nanocomposites has an obvious enhancement to the flexural strength. As a result of the two opposite effects, the flexural strength of silicic acid sol filled PMMA nanocomposites is improved.



Fig. 20. Flexural strength of different PMMA nanocomposites [14].

3.3.7 Others

Scanning Tunneling Microscopy (STM) is a microscope based on the principles of electron tunneling. Between two closed conductors (typically only a few Å) electrons can pass through the barrier between two conductors and flows under external electric field, which calls the tunnel effect. This electrons produce measurable current, the value and the distance between the conductors has exponential relationship: $I \propto \text{Vexp}[-C(\phi S)1/2]$ where I-tunneling current, V-added voltage between conductors, ϕ -effective tunneling barrier (eV), C-constant, S-2 conductor spacing (Å). STM is precise enough to control the positioning of

individual atoms on the probe, and can scan atom one by one in atomic array, which provides atomic resolution of surface analysis.

The main feature of Atomic Force Microscopy (AFM) is that it does not require the surface conductivity, because it measures the scanning probe and the interaction between the tip of AFM and the sample surface. The interreaction includes electrostatic, van der Waals, friction, surface tension (capillary) and the magnetic force, which overcomes the inadequacy of the STM. Unlike the STM, a force map can be obtained from the AFM probe. This map can be interpreted as a reflection of the surface structure and a geometric topology map of magnetic and electrostatic forces.

In addition to the above spectroscopic methods, there are still a variety of other methods, such as Mössbauer spectroscopy, surface analysis spectra and dynamic structure spectroscopy. As is well known, the surface analysis and surface characterization methods are more than 100 kinds. This shows the difficulty of surface characterization. When one characterizes the surface and its structure, it is necessary to integrate different analysis and characterization methods to complement and confirm each other.

4. Application of polymer-inorganic nanocomposites

4.1 Applications of Bi-YIG films and Bi-YIG nanoparticles doped PMMA

Bi-YIG films and Bi-YIG nanoparticles doped PMMA nanocomposites are the functional materials with magneto-optical effects from the ultraviolet to the infrared band ray. With profound investigation of Faraday rotation and gradual recognition of the importance of the effect, people began to take advantage of this effect in practical applications. Various magneto-optical devices prepared using the magneto-optical materials have been widely used in the field of optical communication and optical storage. Magneto-optical modulator, magneto-optical switcher, magneto-optical isolator, magnetic optical circulator, magneto-optical rotator and magneto-optical phase shifter have been invented since 1966.

With the development of optical fiber communication and integrated optics, the integrated magneto-optical waveguide-type device was invented in 1972. The firstgeneration magneto-optical disc was launched in 1988, which has many distinct advantages, such as high-density recording (107 \sim 1010 bit/cm²), erasable writing, rewritable, etc. In addition, the materials with magneto-optical effect are also widely used in the field of magnetic field measurement, high-voltage transmission lines and current measurement sensors, and magneto-optical storage. As the core material of the magnetooptical devices, magneto-optical materials determined the merits of the performance of devices directly. Magneto-optical device has high sensitivity, strong anti-interference, high insulation, low cost, small size, light weight and so on. The material is also widely used in the fields of space, guidance, and satellite monitoring and controlling. Take the advantage of the independent of the magnetic rotation direction with the incidence light direction, the materials can be made into a single-pass optical gate and modulator. The magneto-optical glass with high Verdet Constant (also known as Vd values) can be used for the measurement of high current to prevent accidents caused by lightning and shortcircuit of electrical devices.

Magnetic nanoparticles with magneto-optical effect have important applications. Polymethyl methacrylate (PMMA) doped with these nanoparticles demonstrates magneto-

optical effect and can be used to prepare a variety of devices. The following are some of the mature applications.

4.1.1 Magneto-optical sensor

Magneto-optic sensor is a device to take advantage of magneto-optical effects to detect the changes in magnetic field or current strength. It combines laser, optical fiber and optical techniques in one. It is widely used in high-voltage network testing, monitoring, precision measurement, remote control, telemetry and automated control systems.

The typical structure of a current sensor using optical fiber is shown in Fig. 21. The working principle is: the light sent off by a laser through the polarizer becomes linear polarized light, then the linear polarized light transmits through the optical fiber which winds around the electrical wire. As a result of the Faraday rotation, the polarization angle of linear polarized light deflects. Owing to the changes of light intensity, the analyzer detects the change of the linear polarized light intensity caused by the Faraday deflection, so the actual current can be measured. Traditionally, high-voltage measurement and monitoring used the oil-filled magnetic flux current transformer (OFMFCT). The transformer used much copper wire, insulation materials and machining parts. Compared with OFMFCT, the magneto-optical sensor has some benefits, such as a simple structure, small size and low cost. It is considered to be the most promising high-voltage and high-current measuring devices.



Fig. 21. The structure of a current sensor using optical fiber.

4.1.2 Tuned filter

YIG tuned filter is a device for filtering. A YIG small ball, as the oscillator, selects input signal through the resonant frequency generated by coupling. It works in the frequency range of $3 \sim 40$ GHz, and 3 dB bandwidth can be adjusted between $5 \sim 70$ MHz. Having a very wide frequency tuning range (up to several octave), the YIG is widely used in broadband MW, millimeter-wave receiver for tracking and pre-selecting RF signals.

In the MW frequency, the YIG molecules have a magnetic moment. Normally, the moment was randomly arranged. When a static magnetic field is applied, the magnetic moment will be arranged towards a certain direction. If an alternating magnetic field is applied, the moment will change back and forth. The oscillation frequency is the function of the properties of YIG materials (e.g., magnetic properties, crystall shape and size), and the intensity of magnetic field. The maximum amplitude that appears in alternating magnetic fields exactly equals to the oscillation frequency of YIG crystal. Therefore, we can take advantage of this resonance phenomenon to create filters, as shown in Fig. 22.



Fig. 22. The using of resonance phenomenon to create filters.

A typical YIG resonator constitutes a highly polished YIG sphere with a diameter of $0.25 \sim 0.5$ mm. A small ball is put in the static magnetic field with the field strength of *H*. When a signal enters the input side, the ball produces a circular polarized magnetic moment around the small ball if the signal frequency is equal to the resonant frequency of resonator. When the magnetic field couples with the output coil, the energy generates from the output coil. Otherwise, the small ball is not inspired and no energy is generated.

4.1.3 Magneto-optical recorder

The principle of magneto-optical recording was proposed early in the nineteen fifties, but its specific application was developed in recent years. Magneto-optical recording is the most advanced information storage technology, which combines the advantages of both magnetic disk and CD-ROM. Magnetic discs are widely used in many applications that require large-scale real-time data collection, recording, storage and analysis. The magneto-optical storage systems will replace the traditional storage methods.

Magneto-optical recording technology stores information by heating the small magnetic area to change the orientation of magnetization vector, and then reads out the information using magneto-optical effects. In practical application, the thin and amorphous film placed in reverse magnetic field was heated by a laser beam, resulting in magnetization perpendicular to the membrane surface. Information can be written onto the magnetic domain, and read out by magneto-optic Kerr effect. The most important characteristics of the magneto-optical recording material is that magnetic recording medium should be perpendicular to the membrane surface, and can maintain the stable structure of the small magnetic domain. The magneto-optical Kerr rotation angle of the materials must be large, and reflectivity must be high to enough to achieve high sensitivity and low noise. Moreover, the chemical structure must be stable, and the large film can easily be produced.

A practical magneto-optical recording medium must have the following features: the magnetic anisotropy perpendicular to the membrane surface, and the $K_{\alpha} > 2\pi M_2$ s; a rectangular hysteresis loop (Mr/Ms=1) and high coercivity at room temperature; high magneto-optical recording sensitivity (lower laser recording power); large magneto-optical effect (a large Kerr angle θ_k or large Faraday angle θ_F); low disk writing noise (no big grain); high enough reading and writing cycles; good oxidation resistance, corrosion resistance and long-term stability; Curie temperature between 400 ~ 600 K and compensation temperature at 25°C. In the last two decades, a new magneto-optical material through the replacement of old ones, the current rare-earth transition metal (RE-TM) materials, magneto-optical disc has been put into the market. However, owning to its weak magneto-optical effect, chemically unstable, high price, as well as poor magneto-optical effects near ultraviolet, people began to explore the next generation materials. Bi, Ga substituted Yttrium Iron Garnet magneto-optical material as a new generation of magneto-optical materials has been researched and developed.

4.1.4 Magneto-optic modulator

Magneto-optic modulator modulates light beam by rotating the polarization plane of the incidence light through the magneto-optical medium. The modulator has a wide range of applications, e.g., infrared detectors chopper, infrared radiation pyrometer, TV signal transmission and distance measuring devices, optical detection and transmission system. The structure and working principle of magneto-optical modulator is illustrated in Fig. 23.



Fig. 23. The structure and working principle of magneto-optical modulator.

There is no external magnetic field in the absence of modulated signals. When a beam of intensity I_0 goes through the polarizer, the output intensity is as follows according to Malus law:

$$I = I_0 \cos 2\alpha$$

where *a* is the angle between the optical axis of polarizer and the analyzer. When the two optical axis is parallel (a = 0), the light intensity *I* is maximum. When the two polarizers is perpendicular to the beam ($a = \pi/2$), the light intensity *I* is zero (the output is extinct). When the alternating signal is applied on the electrical coils of magneto-optical materials, an alternating magnetic field is generated and the polarization plane of light is thus rotated. The output light intensity is as follows:

$I = I_0 \cos 2(\alpha \pm \theta)$

when *a* is constant, the output light intensity is only changed with θ . Due to the Faraday rotation effect, the signal current modulates the rotation signal of polarized light into intensity signal. Modulation information was carried by the output light in the form of intensity changing.

During the production of magneto-optic modulators, it requires that the magneto-optical materials should have high transparency and large Faraday rotation (Faraday rotation angle per unit length). The magneto-optical glass was previously used. Currently, the YIG was invented, which has high transparency and high Faraday rotation angle in the 1.1 ~ 5.5 μ m wavelength. As the single-crystal epitaxial thin film magneto-optical material, the Bi-dope YIG is more suitable for preparing the optical modulator. The Faraday rotation angle of the device is as high as $10^3 \sim 10^4$ rad/cm, while the transparency to visible light is still high. For more applications of Bi-YIG, please read section 3 of our recent book [30].

4.2 Application of magnetic Fe₃O₄ based nanocomposites

With the development of industry, waste water from many industries such as chemical manufacturing, mining, battery manufacturing industries, etc., contains toxic heavy metals, which are not biodegradable, causing various diseases. For instances, chromium is present in effluent waters from several different industries. It affects human health, accumulates in the food chain and causes many ailments. Contact with chromium results in severe health problems such as simple skin irritation and lung carcinoma [31]. Strong exposure to Cr(VI) could cause cancer in the digestive tract and lungs, epigastric pain and nausea. Copper is the most important and frequently used metal in industries such as plating and petroleum refining. The industries mentioned above produce much wastewater and sludge containing a high concentration of copper cations, which have negative effects on the environment [32]. The problems of Cadmium and the solutions of its compounds have been found from longterm exposure and work with cadmium plating baths. Uniformity, nickel sulfide fume is recognized as a carcinogenic material. At the same time, the requirement of Ni-Cd batteries has been growing visibly in recent years. It means that there will be enhanced potential for an increasing content of Ni and/or Cd in water. Hence, it is very important to purify water before being used as it is one of the basic demands for the survival of human. And the effective disposal of heavy metals has arouse worldwide concern in the last few decades.

Nowadays, various treatment techniques have been used to remove the metallic ions from the wastewater, such as precipitation, evaporation, solvent extraction, ion exchange, reverse osmosis, membrane separation. Most of these methods suffer from some drawbacks such as high capital and operational costs for the treatment and disposal of the residual metal sludge [33-35]. Therefore, great efforts are taken to develop low-cost materials for removing contaminants from aqueous solutions. Thankfully, recent development of nano-technique has made great progress on this field. Nanoparticles, characterized by a significant amount of surfaces, have got a great deal of attention, because of their unique properties and potential applications.

For an instance, magnetic Fe₃O₄ nanoparticles have attracted much attention not only in the field of magnetic recording but also in the areas of medical care and magnetic sensing [36-38]. It is believed that magnetic nanoparticles exhibit the finite-size effect or high ratio of surfaceto-volume, resulting in a higher adsorption capacity for metal removal. In addition, the easy separation of metal loaded magnetic adsorbent from solution can be achieved using an external magnetic field. Thus, an efficient, economic, scalable and non-toxic synthesis of Fe₃O₄ nanoparticles is highly preferred for potential applications and fundamental research [39-41]. Several recent studies sought to adsorb heavy metals onto magnetic nanoparticles. For example, the removal and recovery of Cr(VI) has been achieved by synthesized maghemite (y-Fe₂O₃) nanoparticles, and it is proved that Cr(VI) adsorption capacity of nanoscale maghemite compared favorably with other adsorbents like activated carbon and clay [42,43]. Very interestingly, a further study from the same group suggests that the Cr(VI) adsorption onto the δ -FeOOH-coated γ -Fe₂O₃ is mainly controlled by the outer-sphere complexation [44]. They also proved that the Cr(VI) can be effectively removed from synthetic wastewater using surface modified jacobsite nanoparticles, in which the adsorption process followed by magnetic separation leads to the rapid, effective and inexpensive removal of toxic ions [45]. The results from another group have shown that magnetic nanostructured particles y-Fe₃O₄ can be successfully applied to adsorb metal ions, in which the combined technique of biosorption and magnetic separation holds the advantages of flexibility, eco-friendly characteristics and economic in operational cost [46]. Recently, a successful removal of Cr(VI) has been achieved by electro-coagulation with Fe electrodes [48]. Of course, there are many other applications, such as protein separation and cell separation.

For more applications, please read section 7 of our recent book [47].

4.3 Application of ZnO based nanocomposites

Nanosized ZnO has a bright future for being used in preparing solar cell, gas sensors, chemical absorbent varistors, electrical and optical devices, electrostatic dissipative coating, catalysts for liquid phase hydrogenation, and catalysts for photo-catalytic degradation instead of titania nanoparticles. Hence, investigations on the synthesis and modification of nanosized ZnO have attracted tremendous attentions.

4.3.1 Gas sensing materials

ZnO has high chemical stability, low dielectric constant, large electromechanical coupling coefficient, ZnO materials have been widely used as dielectric ceramic, pigment, catalyst and sensing material [48]. As a gas sensing materials [49], it is one of the earliest discovered and the most widely applied oxide gas sensing material. It is sensitive to many kinds of gases, and has satisfactory stability. Its gas selectivity can be improved by doping additives and catalysts. But its working temperature is rather high, normally 400-500°C, and its gas selectivity is poor. In recent years, the studies on ZnO gas sensing materials, which can improve its preparation method and decrease its working temperature, are one of its major research topics [50].

4.3.2 Photocatalyst for degradation of organic dye

The use of semiconductor colloids as photocatalyst for a variety of chemical reactions, due to their peculiar optoelectronic photocatalytic properties, is well stated in the recent literatures

[51-53]. The effectiveness of the photodegradation processes has already been tested for different types of matrices and results have been encouraging, as the literature reports on a large number of successes in the degrading of organic dyes in waste water [54]. Under photo-excitation semiconductors undergo charge separation and initiate oxidation of the organic compounds at the interface. Nanostructured semiconductors are a potential candidate to photodegradation of organic compounds because of the size-dependence of their band gap [55], when the semiconductor nanocrystal size is comparable or smaller than the bulk exciton diameter. Therefore, photocatalytic electron and hole redox potentials of size quantized semiconductor nanocrystals can be tuned to achieve increased catalytic effect for selective photochemical reaction. Moreover, as photocatalytic reaction occurs at nanoparticles surface, nanosized semiconductor high surface to volume ratio will contribute to increase the decomposition rate.

Synthetic routes using the principles of colloidal chemistry provide the possibility of separate nucleation from growth, avoiding particles aggregation and controlling their growth. In this paper, nanostructured TiO_2 and ZnO were prepared using new non-hydrolytic methods [56]. These preparative approaches are based on the rapid thermal decomposition of molecular precursors in the presence of strong coordinating agents to produce high crystalline, redispersible, nanosized semiconductor particles, with controllable size and size-distribution. The reactions occur at high temperatures in anhydrous organic solvents, providing oxide nanoparticles with no surface hydroxyl groups, which are known to significantly influence surface oxidation power as well as to decrease interfacial electron-transfer rates with respect to their dehydroxylated counterparts. After optical and structural characterization, the obtained nanoparticles were immobilized onto transparent support in order to exploit them in a photocatalytic process devoted to the photodegradation of methyl red, an organic dye. Then a comparison between the efficiency of nanocatalysts and their equivalent commercial oxides were performed. The obtained results showed a high efficiency.

4.4 Application of magnetic fluid

Magnetic fluids, which are colloidal suspensions of magnetic nanoparticles stabilized by coating surfactants, have attracted much interest recently. Magnetic fluids have been widely used in loudspeakers, hard discs, dynamic sealing, electronic packing, mechanical engineering, aerospace, bioengineering, biological and medical diagnosis and therapy, pharmacy and biosensors.

Sealing techniques of magnetic fluid take advantage of the response of magnetic fluid in a magnetic field. When a magnetic fluid is placed into a gap between the surfaces of rotating and stationary elements in the presence of magnetic fluid, it assumes the shape of a "liquid O-ring" to completely fill the gap.

The magnetic fluid vacuum rotary feed through is a device that transmits rotary motion into a vacuum chamber. The basic components are permanent magnet, two pole pieces, a magnetically permeable shaft and magnetic fluid. The shaft (of pole pieces) contains a multistage structure, completed by the pole pieces and the shaft, concentrating magnetic flux in the radial gap under each stage. In the ideal situation, all flux lines are confined under each stage, and none are in increase region. The magnetic fluid is trapped and held in each stage, forming a series of "liquid O-ring" with intervening regions that are filled with air. Each stage can typically sustain a pressure differential of 0.15 - 0.2 atmosphere. All stages act in series to provide a total pressure capability for the seal. For vacuum applications, magnetic fluid seals are normally designed to sustain a pressure differential of greater than two atmospheres, thus allowing a safety margin. In our researches, biocompatible magnetic fluids based on dextran-coated Fe_3O_4 magnetic nanoparticles was prepared through a one-step method [57]. In contrast to the conventional co-precipitation method, hydrazine hydrate was added as reducing agent and precipitator in the present investigation. The prepared biocompatible magnetic fluids was intravenously injected into rabbits, the iron content in blood and organs at different times were measured by atomic absorption spectrometer, and the bio-distribution and the bio-transportation of magnetic fluids in organs was examined. Then, the magnetic resonance (MR) images of liver, marrow and lymph (as shown in Fig. 24.) were acquired by MRI experiments before and after intravenous injection of magnetic fluids. Image analysis revealed that the MR signal intensity of these organs notably decreased after being intensified by magnetic fluids. However, when there existed tumors in organs, the signal intensity of tumor did not change after injection. From that the tumor can easily be identified, which indicated a potential an application of the as-prepared magnetic fluids in functional molecular imaging for biomedical research and clinical diagnosis.

t(h)	Blood	Lymph	Liver	Spleen	Lung	Heart
	(mg/g)	(mg/g)	(mg/g)	(mg/g)	(mg/g)	(mg/g)
0	0.048	0.010	0.079	0.297	0.038	0.042
0.5	0.255	0.019	0.08	0.316	0.056	0.047
1	0.275	0.02	0.23	0.931	0.093	0.056
2	0.256	0.053	0.188	1.028	0.137	0.095
3	0.14	0.154	0.169	0.656	0.152	0.091
6	0.105	0.206	0.14	0.652	0.097	0.072
9	0.081	0.073	0.113	0.598	0.061	0.071
12	0.050	0.07	0.106	0.594	0.042	0.063

Table 5. The Fe contents in some organs of rabbits at different times [23].



Fig. 24. MR signals intensity of lymph of rabbit in T1-weighted sequences (A and B) and T2-weighted sequences (C and D). Images were acquired before (A and C) and 6 h after intravenous injection of Fe₃O₄ MNPs (B and D) [58].

For more application of magnetic fluid in industry, biotech and pharmaceutical fields, please read section 7 of our recent book [47].

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The Sol-Gel Route to Nanocomposites

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1. Introduction

Nanocomposites are multiphase materials where one of the structural units, either organic or inorganic, is in a defined size range 1-100 nm. In order to prepare organic-inorganic nanocomposites either the particles or the polymers or both can be synthesized "in situ" or used in the final state. When dispersing the nanoparticles, the need of lowering the interface free energy would lead to their agglomeration. Alternatively interactions between inorganic particles and matrix polymer or between particles and an ultrathin layer of surrounding organic molecules must be set up. This is commonly indicated by saying that the inorganic nanoparticles must be compatibilized (Kickelbick 2007). When organic reactive groups are present at the surface of the nanoparticle allowing attachement of matrix polymer molecules, a firm polymer-particle interface can also be obtained. The proper nanoparticle surface engineering can give:

- 1. good dispersion of NP into polymer at high filler content
- 2. adjustment of rheology at high filler content
- 3. covalent bonds between filler and polymer and higher network density
- 4. Materials with improved mechanical properties (fatigue strength, toughness, scratch resistance...) and flame retardancy and coatings with barrier properties

Recently numerous synthesis methods were explored and successfully used to produce organic-inorganic hybrid nanoparticles with controlled defined shapes (core-shell, multinuclear, hairy-like raspberry ...), nanoscale sizes, structure and composition. They have potential applications in a variety of domains, starting from their use as components of advanced both functional than structural nanocomposite materials, where, as reminded above, the engineering of the interface is critical to have good dispersion and for the tailoring of the final properties.

The paper will show that the Sol-Gel method is an outstanding route to the synthesis of hybrid nanoparticles and nanocomposites. Generally speaking it gives inorganic high purity materials at mild synthesis conditions (temperature and pH). An outstanding variation is the so called Stöber method allowing colloidal particles (with well-defined size and shape and with narrow size distribution) be produced through hydrolysis and polycondensation of silicon alcoxides in water /alcohol /ammonia mixtures. The sol gel method allows, also, easy functionalization of silica nanoparticles with specific organic groups. Many of the hybrid nanoparticles synthesis methods take advantage of all this. The sol gel method finds, however, applications in many other research fields. The aim of this paper is to give also, shortly, a contribution to the knowledge of the basic principles of the method, with

particular reference to the synthesis of functionalized silica nanoparticles through the Stöber method.

The paper is structured in six sections, the first one being the introduction. In the second a brief outline of the sol-gel process and the basic principles of the sol stability are reminded; the types of possible precursors are also shortly described. The third section is devoted to the silicates Sol-Gel chemistry, showing concepts that can be extrapolated to the other precursors. In the fourth section the Stöber method and its mechanism are treated. In the fifth the relevant applications to the synthesis of organic-inorganic hybrid nanoparticles and to nanocomposites are addressed.

2. Sol-gel method general remarks

2.1 Brief outline of sol-gel process

The sol-gel process is a synthesis route consisting in the preparation of a sol and successive gelation and solvent removal. The precursors, better described in the successive paragraph, consist of a metal or metalloid element surrounded by various ligands. Very popular are the metalorganic compounds used in the synthesis of silicates, like tetraethyl silicate (or tetraethoxy-silane) Si(OC₂H₅)₄, shortly indicated with the acronym TEOS. Very often organometallic compounds are used having some of the alcoxide groups substituted with other organics, having carbon directly bound to silicon, like methyltriethoxy-silane CH₃Si(OC₂H₅)₄.

The use of silicon metalorganic and organometallic compounds is reported in a great number of papers (Brinker 1990). The hydrolysis and polycondensation reactions are very useful to obtain both polymeric (containing no dense oxide particles larger than 1 nm) than particulate silicate sols:

$$\operatorname{Si}\left(\operatorname{OR}\right)_{4} + n \operatorname{H}_{2}\operatorname{O} \rightarrow \operatorname{Si}\left(\operatorname{OR}\right)_{4-n}\left(\operatorname{OH}\right)_{n} + n \operatorname{ROH}$$
(1)

$$\equiv \text{Si} - \text{OH} + \text{HOSi} \equiv \rightarrow \equiv \text{Si} - \text{O} - \text{Si} \equiv +\text{H}_2\text{O}$$
(2)

$$\equiv Si - OH + ROSi \equiv \rightarrow \equiv Si - O - Si \equiv + ROH$$
(3)

Polycondensation turns monomers into oligomers and, finally, polymers.

As long as the number of alcoxide groups, (therefore the number of bonds the monomer can form, that is the "functionality"), is greater than 2, complex random branching may occur finally leading to fractal structures. Euclidean objects ($m \propto r^3$, where m is the mass and r is the radius), instead, form in systems in which the particle is partially soluble in solvent: monomers can dissolve and reprecipitate until structures having minimal interfacial area form.

The fractal aggregates grow until they begin to impinge on one another and bonds form at random, linking them in a network and giving a gel. This is therefore a substance containing a continuous solid skeleton enclosing a continuous liquid phase. The "gel point" is reached when a "spanning cluster" appears extending throughout the sol. Initially it coexists with many smaller clusters present in the sol phase. However these progressively become attached to the network giving a monolith.

The gel "aging" involves important processes: condensation, dissolution and reprecipitation. Therefore it strongly affects the final structure and properties. Usually, at

first, syneresis occurs: contraction with expulsion of liquid from the pores. Drying by evaporation gives "xerogels" having a volume 5 to 10 times smaller of the original gel volume. Drying under supercritical conditions ("supercritical drying"), in autoclave, gives aerogel with relatively little shrinkage.

Successive thermal treatments give dense ceramics, both crystalline than amorphous.

In some experimental conditions stable sols are obtained and nanoparticles can be, therefore, produced as discussed at length in the following.

The sol-gel method is very versatile, allowing to easily obtain not only bulk samples and nanoparticles but also films and fibers.

2.2 Types of precursors

Metal (Si, Ti, Zr, Al, B...) alkoxides precursors are largely used (Brinker 1990). The reactions are all similar to the ones above reported for silicon alkoxides. The mechanism are also similar to the ones described, in the following, for the silicon alkoxides, based on nucleophilic attack to the central atom.

Inorganic salts are, also, very often used (Brinker 1990, Livage 1988). Salts in water give, in fact, solvated cations. The charge transfer from the bonding orbitals of water molecules to empty d orbitals of transition metal makes the water molecule more acidic. Different complexes can form depending on the magnitude of electron transfer:

$$\begin{bmatrix} M - OH_2 \end{bmatrix}^{z^+} \rightarrow \begin{bmatrix} M - OH \end{bmatrix}^{(z^{-1})^+} + H^+ \rightarrow \begin{bmatrix} M - O \end{bmatrix}^{(z^{-2})^+} + 2H^+$$

aquo - ion, hydroxo - ion oxo - ion

When the water molecules number is N, also hydroxo-aquo and oxy-hydroxo ions may form. The general formula of the complex is:

$$\left[MO_{N}H_{2N-h}\right]^{(z-h)+}$$

Where aquo ions correspond to h=0, hydroxo ions to h=N, oxy ions to h=2N, hydroxo-aquo when $[1 \le h \le (N-1)]$, oxy-hydroxo when $[(N+1) \le h \le 2N-1]$

The nature of the complex depends on: charge, *z*; pH of the solution; coordination number, N; electronegativity, number of metal ions bridged by hydroxo or oxo ligands; number of H atoms in the ligand; number of OH coordinating M

The dependence on the charge and pH of the solution is roughly described by the diagram of Fig.1 giving the rough limits of existence of the various complexes

Condensation can occur by Nucleophilic substitution mechanism (SN) (when the preferred coordination is satisfied)

$$M_1 - OX + M_2OY \rightarrow M_1 - OX - M_2 + OY$$
 (4)

Or through nucleophilic addition (AN) (when the preferred condensation is not satisfied):

$$M_1 - OX + M_2OY \rightarrow M_1 - OX - M_2OY$$
 (5)

It is generally necessary to be in the hydroxo domain to generate condensed species. The exception is the case of coordinatevely unsaturated oxo-precursors. Changes of pH through addition of bases or acids, reduction of oxo-precursors or thermohydrolysis allow to move into the hydroxo domain.



Fig. 1. The charge-pH diagram (from Livage 1988)

It's worth reminding that a predictive model for inorganic polymerization reactions was proposed (Livage 1988) based on the electronegativity concept introduced by L-Pauling as well on the principle of electronegativity equalization suggested by R.T.Sanderson (Sanderson 1951). The model works quite well (Brinker 1990, Livage 1988) to predict ionic and condensed species in the case the precursor is an inorganic salt so as the products of hydrolysis and condensation reactions of metalorganic precursors.

2.3 SOL stability

Nanoparticles are obtained, as previously reminded, when stable sols are formed during the hydrolysis and polycondensation of sol-gel precursors. Because of their very high specific surface area, nanoparticles have a themodynamic strong tendency to agglomerate to reduce surface energy.

The dispersion forces (Mahanty 1976) are the attractive ones responsible of flocculation. At atomic level the dispersion energy depends on the sixth power of the distance. Slower changes with the distance occur in the case of nanoparticles. Aggregation can be avoided through electrostatic and/or steric barriers due to electrostatic repulsion of surface charges and/or adsorption of organic molecules.

The DLVO theory (Parfitt 1981, Brinker 1990) successfully describes the stabilization due to electrostatic repulsion. The surface of oxide particles is positively or negatively charged because of the action of the "charge determining ions", H⁺ and OH⁻:

$$M - OH + H^+ \rightarrow M - OH_2^+ \tag{6}$$

$$M - OH + OH^{-} \rightarrow M - O^{-} + H_{2}O$$
(7)

A "Point of Zero Charge" (PZC) is defined as the pH at which the particle has no electric charge. Because of eq. 6 and 7 the particle is positively charged at pH<PZC and negatively

charged at pH>PZC respectively. PZC for silica is pH≈2; therefore, but in the case of very acid solutions, the surface has a negative charge due to reaction 7; this negative charge is greater the higher is the departure of pH from PZC. A surface potential, Φ_0 , settles whose value also depends on the departure of pH from PZC. Counterions are, therefore, strongly attracted from the solution; altogether with water molecules they form the tightly bound "Stern layer" around the particle. The plane separating the "Stern layer" from the "Gouy layer", containing freely diffusing ions, is called Helmoltz plane. Another plane is individuated, the so called "slip plane": it separates, inside the Gouy layer, a inner part that moves with the particle during electrophoresis. The counterions screen the surface electrical charge, making the electrostatic potential to decrease; the decrease is linear inside the Stern layer but follows, in the Gouy layer, the law:

$$V_{\rm R} \propto \exp - \left[k \left(h - H \right) \right] \tag{I}$$

Where h is the distance from the surface (H being the distance of the Helmoltz plane) and

$$\mathbf{k} = (\mathbf{F}^2 \sum (\mathbf{c_i} \mathbf{z_i}^2) / \epsilon \epsilon_0 \mathbf{R} \mathbf{T})^{\frac{1}{2}}$$
(II)

where F and R are the Faraday and universal gas constants, ε and ε_0 are the dielectric constant of the solvent and the permittivity of vacuum, c_i and z_i are the charge and concentration of counterion of type i.

The potential on the sleep plane is called the ζ -potential, $\Phi_{\zeta'}$ and the pH at which $\Phi_{\zeta}=0$ is the Isoelectric Point (IEP), often taken equal to PZC.

The reverse of k is called the Debye-Huckel screening length and is a measure of how much the repulsive potential extends far apart from the surface.

Following the DLVO theory, the potential energy near the surface of a particle is the sum of Van der Waals attractions and electrostatic repulsion potentials shown in Fig. 2 (from Parfitt).

Therefore it depends on the Debye-Huckel screening length as shown in Fig 3 (from Parfitt).

However it depends also on the radii of the two approaching particles, as shown by fig 4 (Parfitt).

The stability of the sol depends on the height of the maximum of the total potential energy. Therefore:

- a. the sol stability decreases in the presence of salts (the more the higher the concentration).
- b. Monodisperse particles are more stable than polydisperse ones.

c. The stability increases with the size of the particles.

Recently another attractive (Ping 2006) force was recognised to be active, the so called depletion force. A simple interpretation (M.Singh-Zocchi 1999) of the nature of these forces is based on the concept of osmotic pressure. It occurs when particles of radius R are dispersed in a liquid in the presence of a cosolute consisting of spherical polymeric particles of gyration radius r_p , that are not able to bind to the particles surface. When two or more particles come close enough to overlap the shells of thickness r_p , the polymeric particles are excluded from the space between them (the depletion zone). The osmotic pressure acting on the excluded volume gives rise to an attractive force and drives the particles closer.



Fig. 2. DLVO potential representation: V_A : attractive Van der Waals potential; V_R repulsive electrostatic potential (from Parfitt 1981)



Fig. 3. Influence of electrolyte concentration on total potential energy of interaction of two spherical particles of radius 100 nm in aqueous media: a) $1/k = 10^{-7}$ cm; b) $1/k = 10^{-6}$ cm; c) $1/k = 10^{-5}$ cm; d) $1/k = 10^{-4}$ cm; (from Parfitt 1981)



Fig. 4. Theoretical curves of total potential energy against distance of separation of two spherical particles of radii a_1 and a_2 and equal surface potential (35.86 mV); $1/k = 10^{-6}$ cm (from Parfitt 1981)

a): a₁=125 nm and a₂= 125 nm (1), 100nm (2), 75 nm (3), 50 nm (4) 12.5 nm (5)

b): a₁=12,5 nm and a₂= 125 nm (1), 100nm (2), 75 nm (3), 12.5 nm (4)

Steric barrier occurs, instead, when a thick layer of organic molecules is adsorbed (Sato 1980, Napper 1983). The need of the following conditions is recognised (Tadros 1982) for an effective steric barrier:

- a. the particle surface should be completely covered
- b. the polymer should be firmly anchored to the surface
- c. the layer must be thick enough to have the particles at a distance where the Van der Waals attractions are weak
- d. the nonanchored polymer segment must be well solvated

When the particles possess an electric charge or the polymers are polyelectrolytes an electrosteric barrier settles (Napper 1983).

Recently it was claimed (Gao 2009, Branda 2010) that in some cases polymer coated inorganic nanoparticles, a few nm in diameter, could form stable nanometric clusters of the kind represented in Fig. 5

The observed need of an optimal polymer/nanoparticle mass ratio for the long term stability can be explained (Branda 2010) by admitting that both steric than electrostatic stabilization occurs. In this case the polymer is expected to play a double role: at level of cluster formation and successive cluster aggregation. The polymer content increase makes, of course, the steric hindrance to increase thus improving stability. However just for the same reason, as illustrated in Fig.5, the number of silica particles per unit volume in the cluster is expected to decrease, by this way reducing the electrostatic hindrance among clusters and improving the tendency to cluster aggregation. Therefore the need for the stabilization of an optimal polymer/nanoparticle mass ratio was justified.





3. Silicates sol-gel chemistry

3.1 Aqueous silicate chemistry

Although 4+ is the only silicon important oxidation state and 4 is its most important coordination number, aqueous silicate chemistry is very complex.

When dissolving silicates in acidic solutions the formation of silicic acid would be expected:

$$Na_2SiO_3 + H_2O + 2HCl \rightarrow Si(OH)_4 + 2Na^+ + 2Cl^-$$

It was early observed that (Freundlich 1926) the silicic acid solutions slowly thicken and finally give a gel. This was explained by Iler (Iler 1979) through a polymerization mechanism in three steps: formation of particles from the monomers, successive growth of them and establishment of links giving chains and networks extending throughout the liquid medium.

²⁹Si NMR (Harris1982, Knight 1988)) allowed, effectively, to identify numerous silicate species (from dimers to prismatic hexamers) present in aqueous silicate solutions. Rings appear to easily form as a result of a tendency to maximise the number of siloxane Si-O-Si bonds and minimise the number of terminal hydroxyl groups. Nanosized particles are, by this way, easily formed. The successive fate (Iler 1979) depends on the synthesis conditions:

- 1. sols when working at pH=7-10 in the absence of salts
- 2. three dimensional gel networks when working at pH<7 or at pH=7-10 in the presence of salts.

This is illustrated in Fig. 6 that shows schematically the overall sol stability and gel time dependence on the pH (Iler 1979).

Two important pH values appear to be: a) the point of zero charge, where the electrical surface charge is zero (changing in the pH range 1-3); b) the pH \approx 7 where both silica solubility and dissolution rate begin to be important.

The gel time maximum at PZC can be explained taking into account the mechanisms of condensation:

1. above PZC:

$$\equiv \text{Si} - \text{OH} + \text{OH}^{-} \rightarrow \equiv \text{Si} - \text{O}^{-} + \text{H}_2\text{O}$$
(8)

$$\equiv \text{Si} - \text{O}^- + \text{HO} - \text{Si} \rightarrow \equiv \text{Si} - \text{O} - \text{Si} \equiv +\text{OH}^-$$
(9)

2. below PZC

$$\equiv \text{Si} - \text{OH} + \text{H}_3\text{O}^+ \rightarrow \equiv \text{Si}^+ + 2\text{H}_2\text{O} \tag{10}$$

$$\equiv \operatorname{Si}^{+} + \operatorname{HO} - \operatorname{Si} \equiv \rightarrow \equiv \operatorname{Si} - \operatorname{O} - \operatorname{Si} \equiv + \operatorname{H}^{+}$$
(11)

As a consequence, according to Fig.6, the condensation rate is expected to increase with pH above PZC and with the H_3O^+ concentration (decreasing pH values) below PZC; therefore a maximum is expected at PZC. Owing to inductive effects, the most acidic silanols are the ones linked to the more highly condensed species; therefore we expect condensation to occur, preferentially, between more highly and less highly condensed species. Highly branched structures are, by this way, expected to form.

However at higher pH other effects become important. In fact (because of reaction 8) the higher is the pH the greater the ionization of the condensed species and, therefore, the negative charge making them mutually repulsive. It's worth reminding, also, that (section II 1) the "spanning cluster" forms as the result of the impingement of the fractal aggregates on one another and formation of bonds at random. Therefore the increase of the gel time above pH=7 can be explained, so as the effect of salts. In fact salts reduce stability furnishing ions screening the surface charge of the particles (see section II 3). The gel time is expected, therefore, to increase above pH 7 the less the higher the concentration of salts. This is in good agreement with Fig.6.



Fig. 6. Effects of pH in the colloidal silica-water system (from Iler 1979)

Moreover, in the pH range 7-10, both solubility and dissolution rate increase. Another growth mechanism is expected to take place. In fact, as solubility decreases when the radius of curvature increases, bigger particles may grow at the expense of the smaller ones (Ostwald ripening mechanism).

Above pH=10 the solubility is too high to allow gel or particles formation.

3.2 Silicates from alcoxides

Silicate gels are usually obtained from alkoxysilanes (eq.1-3). Owing to miscibility problems of water and alkoxysilanes, a mutual solvent must be used; the alcohol corresponding to the alkoxide group of the precursor is usually chosen. A water/silicon ratio (in the following indicated as r) equal to 2 would be required by the stoichiometry of the overall reaction:

$$Si(OR)_4 + 2H_2O \rightarrow SiO_2 + 4 ROH$$

However r values spanning from 1 to more than 50 have been used (Brinker 1982) in reaction media frequently acid or basic. Early works showed that, depending on the experimental conditions (alkoxide concentration, water/silicon ratio and concentration of acid or base), monoliths, films, fibers or monodisperse spheres can be easily obtained (Nogami 1980, Brinker 1982, Stöber 1968, Sakka 1984). A general trend was observed (Brinker 1982): acid catalysed hydrolysis with low r value produces weakly branched "polymeric sols" whereas base catalysed hydrolysis with larger r values produces highly condensed "particulate" sols.

Mechanisms

Both hydrolysis than condensation mechanisms proceed through nucleophile attack to the silicon, catalysed by acid or base.

In the case of acid catalysed hydrolysis it is thought (Pohl 1985, Keefer 1984, Uhlmann 1984) that protonation of an alkoxide group makes it a better leaving group allowing substitution with water:

$$H_2O+Si (OR)_3 (OHR)^+ \rightarrow (H2O)^{\delta^+} \dots Si (OR)_3 \dots (OHR)^{\delta^+}$$
(12)

$$(H2O)^{\delta_{+}} \dots Si(OR)_{3} \dots (OHR)^{\delta_{+}} \rightarrow Si(OR)_{3} OH + ROH + H^{+}$$
(13)

The nucleophile attack may occur on the "opposite side" of the leaving group, as usually in the SN_2 mechanisms, or on the "flank side" involving no inversion of the silicon tetrahedron.

The base catalysed hydrolysis, instead, starts with the nucleophile attack (Iler 1979, Keefer 1984, Pohl 1985) of OH; this causes the displacement of alkoxide group (better leaving group than OH). The transition state is, in this case, negatively charged.

The acid catalysed condensation mechanism (Pohl 1985), as described by eq. 10 and 11, involves protonation of a silanol allowing successive nucleophilic attack. The base catalysed condensation mechanism (Pohl 1985, Voronkov 1978), described by eq. 8 and 9, occurs through the nucleophilic attack of deprotonated silanol

<u>Steric effects</u>. According to the mechanism, the hydrolisis and condensation rates strongly decrease as the chain length or degree of branching of the alkoxy or alkyl groups present in the precursor molecule increase (Voronkov 1978).

<u>Inductive effects</u>. The inductive effect can be easily understood if we take into account that hydrolisis and condensation involve the progressive substitution of -OR groups with -OH

and -OSi ones and occur through mechanisms involving transition states, positively charged in the case of acidic conditions and negatively charged in the case of basic conditions. We must, moreover, take into account that the substituent groups (including also the alkyl ones present in organometallic precursors) have different electron providing (or electron withdrawing) effect and, therefore, affect in a different manner the reactions in acidic or basic medium. The electron providing ability and the stability of transition states change in the sequence:

 \rightarrow

increasing electron providing ability

(increasing stability of positively charged transition states)

(decreasing stability of negatively charged transition states)

As a consequence collected experimental results (Schmidt 1984) can be interpreted:

- Under acidic conditions the hydrolisis rate would decrease with each subsequent hydrolisis step
- Under basic conditions each subsequent hydrolisis step would occur more quickly as hydrolisis and condensation proceeds
- Under acidic conditions the hydrolysis rate of organometallic precursors (RO)4-nSiR'n increases with n
- Under basic conditions the hydrolysis rate of organometallic precursors (RO)4-nSiR'n decreases with n

The silica (SiO₂) isoelectric point (IEP), usually taken equal to the point of zero charge (PZC), is about 2. It is clear that its value is influenced by the presence of electron-providing alkyl groups (reducing the acidity of silanols and therefore increasing the isoelectric point) or electron withdrawing OH or OSi groups (increasing silanols acidity and therefore reducing the IEP). As acid catalysed and basic catalysed condensation mechanisms involve protonated and deprotonated silanols, the base catalysed condensation occurs when the pH is greater than the IEP. In general base catalysed condensation is referred to as occurring starting from pH=2.

The observation that base catalysed condensation occurs preferentially between more highly condensed species and less highly ones can, therefore, be explained. In fact

- Replacement of more electron providing OR groups with progressively more electronwithdrawing OH and OSi groups reduces the nucleophile character
- Replacement of more electron providing OR groups with progressively more electronwithdrawing OH and OSi groups increases the ability to suffer nucleophile attack.

H₂O/Si ratio

The H_2O/Si ratio has a complex effect on the overall process. Of course hydrolisis accelerates as H_2O/Si ratio increases. Moreover the higher value of the ratio causes more complete hydrolisis of the monomers before significant condensation occurs. Two effects on the condensation reactions are easily recognised:

- a. At low ratios the alcohol producing condensation reactions are favoured (reaction 3) while the water producing ones are favoured at high H₂O/Si ratios (reaction 2).
- b. large values of the ratio promote siloxane bond hydrolysis (reverse of condensation reaction 2).

Solvent effect

Protic solvents (water, methanol, ethanol, 2-ethoxyethanol, formamide, etc.) so as aprotic solvents (dimethylformamide, tetrahydrofuran, dioxane 1,4 etc.) have been largely used having very different dipole moments (Brinker, 1982). Both protic and polar character of the solvent molecules affect the hydrolysis and condensation reactions (Brinker 1982).

The solvent dipole moment affects the elctrostatic stabilization and the distance over which a charged catalytic species, i.e. the oxydril nucleophile or hydronium electrophile ions, are attracted to or repelled from potential reaction sites.

Aprotic solvents do not hydrogen bond, therefore do not affect the nucleophile or electrophile character of the nucleophile and electrophile agents involved in hydrolisis and condensation reactions.

Usually the alcohol corresponding to the alkoxyde group of the metalorganic compound is used; this allows to avoid transesterification reactions:

$$R'OH+Si(OR)_{4} \rightarrow Si(OR)_{3}OR'+ROH$$
(14)

Some experimental results (Yamane 1984) would indicate that transesterification proceeds much further under acidic conditions than under basic conditions

4. Silica nanoparticles sinthesys

4.1 The Stöber method

Many methods (Brinker 1990) allow to prepare particles from solution or from vapour phase. One of the most popular is the so called Stöber method (Stöber 1968) allowing to prepare monodisperse silica spheres from less than $0.05 \,\mu\text{m}$ to $2 \,\mu\text{m}$. The method is based on the hydrolysis and polycondensation of alkyl silicates in basic (ammonia) alcoholic solutions, therefore on the sol-gel method reactions 1-3. The particles size strongly depended on the water and ammonia concentration (Stöber 1968), but also on the nature of the alcohol used as a solvent. When using alcohols of higher molecular weigh the reaction was slowed down and both median particle size than the spread of the size distribution increased simultaneously.

The work was extended by Bogush et al. (Bogush 1988). A correlation was found allowing to predict quite well the final particles size, d, over concentrations of 0.1-0.5M TEOS, 0.5-17.0M H_2O , 0.5-3M NH_3 :

$$d = A[H_2O]^2 \exp(-B[H_2O]^{1/2})$$

Where

$$A = [TEOS]^{1/2} (82 - 151 [NH_3] + 1200 [NH_3]^2 - 366 [NH_3]^3)$$

$$B = 1.05 + 0.523 [NH_3] - 0.128 [NH_3]^2$$

The correlation failed particularly at small particle size and high TEOS concentration. The effect of changing the temperature, in the range 9-55°C, was also studied. The final particle size was found to decrease monotonically as temperature increases with progressively narrower sizes distributions. The particles were found to have a porosity of 10-15%.

The solids content achieves (Bogush 1988) a maximum value of 3% at a TEOS content of 0.5M. In order to obtain both larger particles than larger final mass fractions, a "seeded growth" process was proposed (Bogush 1988). In this case the particles obtained through the Stöber method act as seeds. When the Stöber synthesis goes to completion, proper amounts of TEOS and water (in a molar ratio 2) are added. The amounts must not exceed a critical value (depending on the initial particle size and number density and reaction temperature) for which a second population of stable colloidal particles may be formed. The process can be iterated several times. The final average diameter, d, is

$$d = d_0 (V / V_0)^{1/3}$$

where d_0 is the initial average diameter and V and V₀ are respectively the total volume of alkoxide added and the volume of alkoxide used to produce the seed particles.

The method can be applied to alkoxide mixtures however a size effect of the partial substitution of alkoxides was observed (Branda 2007). Stable colloids were obtained when the pure alkoxides, tetraethoxysilane (TEOS) or 3-aminopropyltriethoxysilane (APTS), were used; a surprising particle size increase was observed when mixing TEOS and APTS at constant overall alkoxide content. This size effect was greater the closer was the TEOS/APTS concentration ratio to 1.

The "seeded growth" process and the use of alkoxides mixtures open the way to the ease production of functionalized nanoparticles. This is obtained through the use of organometallic precursors, having some alkoxide groups substituted with other organic groups bound through a direct Si-C bond which is not prone to hydrolysis. The use of APTS, for example, is the main route followed to have reactive amino groups present at the surface of the nanoparticles.

The Stöber method has been extended (Brinker 1982) to prepare nanoparticles of different composition, i.e TiO₂, ZrO2, ZnO, Ta2O5, SiO2 doped B2O3 etc.

4.2 The Stöber method mechanism

The factors affecting the sol stability (section II 3) play a central role in the Stöber method mechanism for which an aggregative growth model is nowadays universally accepted (Bogush 1991). Following this theory primary particles are formed through the sol-gel chemistry (section III) having a maximum diameter 1-10 nm. According to Flory-Huggins (Flory 1953) theory and Tanaka and co-workers (Tanaka 1977, Huchberg 1979) the primary particles size is smaller the poorer solvent is the suspending medium. The other assumption of the mechanism proposed by Bogush are:

- 1. particles grow solely by binary aggregation
- aggregating particles coalesce to form a spherical particle of the mass of the aggregating pair
- 3. primary particles are formed in a constant size at a rate that can be related to the loss of soluble species from the solution and is independent of the amount of gel phase present. This stage is indicated as "nucleation"
- 4. aggregation rates are determined by typical colloidal interaction potentials

Size dependent aggregation rate constants are determined from estimates of particle properties and measures of particle surface potential. The model provides (Bogush 1991) good estimates of final particle size distribution parameters from silicon alcoxide reaction rates. The particle surface potential is considered to be governed by the sum of Van der

Waals, electrostatic and solvation interactions. These last are accounted for due to their importance in the flocculation of silica in aqueous dispersions (Allen, 1969, 1970, 1971). An interesting result of the calculations is that primary particles aggregate with larger ones more rapidly than they do with themselves; moreover larger particles aggregate slowly with particles of similar size. Primary particles production appears to be the rate limiting particle growth step.

The analysis was confirmed by other authors (Lee 1988). A narrow final size distribution can be obtained if the aggregation rate for large/large pairs is slower than for small/small or small/large pairs. The final particle size and density depends on the relative rate of nucleation and aggregation (Lee 1988).

SAXS results showed that (Boukari 1997 and 2000) the primary particles have the same size (Rg≈4nm in methanol and Rg≈10nm in ethanol) and low density structure independent of the ammonia and water concentrations. It was found (Green 2003) that ammonia and water concentrations control the balance between hydrolysis of TEOS and the condensation of its hydrolysed monomers. The first nanostructures appear at a hydrolysed monomer concentration around 0.1M (Green 2003), indicating that formation of the primary structures is thermodynamically controlled by supersaturation of the intermediate species. The differences in the particle size between the solvent and the hydrolized intermediates.

All this allowed to give an explanation (Branda 2007) to the reminded tricking size effect of mixing alcoxides (section IV 1). Nuclei of different size are expected to form when the alkoxides are mixed. The mixing appears to change the evolution of particle population favouring the establishment of a size distribution wherein the dominant aggregation event can be between the freshly generated nuclei and large aggregates, which is the faster aggregation event. The closer is the TEOS/APTS ratio to 1 the sooner particles size differentiation would occur and the fewer but greater particles would form, in short times.

5. Synthesis of nanocomposites

The sol-gel method allows to easily produce inorganic nanoparticles. However, as reminded in the Introduction section, their dispersion into a polymer matrix requires their functionalization (Kickelbick 2007). In fact, in a nanocomposite, the maximum interface free energy per volume of composite, E_{v,max}, is the sum of the free energy of the inorganic particles, γ_i , and the surface energy of the polymer, γ_p , in the vacuum. However γ_i is much higher than γ_p . In a nanocomposite the specific surface area of the particles is very high leading to very high values of $E_{v,max}$. This leads to a strong tendency to agglomeration of particles. This is a very great problem in the synthesis of nanocomposites. Alternatevely (Caseri 2007, Bourgeat-Lamy 2007) it can be decreased by interactions between particles and matrix polymer or between particles and an ultrathin layer of surrounding organic molecules. The tailoring of the interface is, otherwise, also relevant for the final properties of the composite. There is, therefore, a great interest in the synthesis of hybrid organic/inorganic nanoparticles. Many routes were followed to obtain this (Elodie Bourgeat Lamie 2007). In the greater part of them the sol-gel technique plays a central role. The topic was smartly revewed by Bourgeat-Lamie (Bourgeat-Lamy 2007) with a short and quite exhaustive description of examples. They are summarized in the following, where a phew interesting examples are indicated:

- 1. Self assembly of preformed organic and inorganic nanoparticles:
 - heterocoagulation based on electrostatic interactions due to different surface charge of the organic and inorganic particles in colloidal solutions of properly selected pH (Marston 1998)
 - b. layer by layer assembly consisting in the deposition of uniform polymer films onto mineral substrates by the sequential adsorption of polyanions and polycations (Decher 1997, Caruso 1998)
 - c. molecular recognition assembly: the colloidal organization based on the presence of bifunctional mediating molecules bearing reactive groups on both ends capable of bonding particles together (Fleming 2001)
- 2. In situ polymerization in the presence of preformed mineral particles:
 - a. grafting of organosilane and organotitanate coupling agents
 - b. polymerization in multiphase systems. One strategy is the grafting of organometallic compounds (like methacrylate silane molecules (MPS)) that allows anchoring of the growing polymer chains on the mineral surface during the earlier stages of emulsion, dispersion or miniemulsion polymerization (Bourgeat-Lamie 1999 e 2006, Reculusa 2004).
 - c. surface initiated polymerization, that is templating inorganic colloids with polymer brushes in solution (Advincula 2003, von Werne 2001). In the Graft-to technique a functional group of a preformed polymer is reacted with active sites on the inorganic surface. In the graft-from technique polymers are grown, through controlled radical polymerization (CRP), directly from the inorganic surface which has been functionalized with the appropriate initiator or catalyst. Owing to the narrow molecular weight polidisperity assured by CRP the grafted particles can self-organize into 2D arrays with controlled interparticle distances function of the degree of advancement of the reaction
- 3. In situ formation of minerals in the presence of polymer colloids
 - a. sol-gel nanocoating (Imhof 2001) . In this case the polymer nanoparticles are the templates for the sol-gel polycondensation. The synthesis requires the use of appropriate compounds enhancing the coupling. These are either organometallic compounds (like MPS) containing groups capable to undergo a chemical reaction with the organic precursor or ionic molecules able to promote electrostatic attractions
 - b. reaction of previously adsorbed metal salt precursors
 - c. growth of inorganic nanoparticles within a swelling polymer matrix that plays the role of nanoreactor (Mayer 2000).
- 4. Hybrid nanoparticles (organic-inorganic interpenetrated networks (IPN)) through simultaneous reaction of organic monomers and mineral precursors. The rate of both reactions must be not too much different and a coupling agent must be used to link the inorganic network and the organic polymer. Very interesting hybrid colloids with interpenetrated networks (IPN) can be formed. Properties are expected significantly different than a simple combination of the two components ones, controlled by the functionality and connectivity of the molecular precursors

Although very short, the above reported description points out that all the reminded methods require a deep knowledge of the sol-gel chemistry. This is, in fact, fundamental to have nanoparticles with the desired size, structure, composition and right surface properties (electric charge and reactivity); it is also essential to plan and properly control grafting of molecules or the production of organic-inorganic interpenetrated networks.

6. Conclusions

The Sol-Gel route is a versatile method allowing to produce bulk materials, either crystalline or amorphous of controlled porosity, as well as fibers, films and nanoparticles. Also in the rapidly growing and very promising research field of nanocomposites it plays a central role; this is linked to the production of hybrid organic/inorganic nanoparticles. In fact the need to have a good dispersion of the nanophase into the matrix and the interest to proper tailoring of the final properties can be, just, satisfied through the synthesis of hybrid organic/inorganic nanoparticles.

The Stöber method allows to obtain inorganic monodisperse nanoparticles from less than $0.05 \,\mu\text{m}$ to $2 \,\mu\text{m}$; the process involves a growth mechanism based on the aggregation of very fine primary particles; these are obtained through hydrolysis and polycondensation of the classical precursors of the sol-gel method. The sol-gel chemistry controls, therefore, the size, structure, composition and surface properties (electric charge and reactivity) of the Stöber nanoparticles. It is also important to plan and properly control grafting of molecules or the production of organic-inorganic interpenetrated networks. Its deep knowledge is, therefore, essential to plan and control the production of organic inorganic hybrid nanoparticles.

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Part 2

Electrochemical Properties

Oxide-Matrix Based Nanocomposite Materials for Advanced Magnetic and Optical Functionalities

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1. Introduction

Advanced engineering applications often require multifunctional materials with a wide range of tunable properties. Such a technological demand is usually difficult to fulfill using single-phase materials. Hence, there is an increasing need to combine materials with dissimilar properties, in a synergetic manner, to achieve certain technological goals. This has prompted the development of novel types of composite materials and the concomitant implementation of innovative processing routes. Examples of currently used composite materials are: polymer-matrix composites, metal-matrix composites or ceramic-metal mixtures (also termed *cermets*), among others (Ajayan et al., 2003).

Some of the properties of composite materials (e.g., mechanical hardness, fracture toughness or coercivity) are often enhanced when their crystalline structure is refined towards the nanoscale. Similarly, physical and chemical properties related to interfacial effects (e.g., magnetic exchange bias or catalytic efficiency), are also improved in nanocomposite structures with respect to coarse-grained multi-component materials. Furthermore, some interesting size effects (e.g., quantum effects) can also emerge in materials whose structure is made nanocrystalline. These novel effects have triggered the interest for *nanocomposite materials*, where at least one of their counterparts shows crystallite sizes typically below 100 nm. Although many of the technological applications of nanocomposite materials benefit from their outstanding mechanical properties, in this work we focus our attention on other types of properties (magnetic and optical) exhibited by a particular type of composite

materials made of an oxide matrix in which either a metal, another oxide or a semiconductor are embedded or in intimate contact. More specifically, we have investigated the properties of nanocomposite materials consisting of: (i) hard ferromagnetic (FM) SmCo₅ particles exchange coupled to an antiferromagnetic (AFM) NiO matrix, prepared by mechanical milling; (ii) mesoporous NiO/NiCo₂O₄/Co₃O₄ composite materials prepared using a multistep nanocasting approach and (iii) CdS-filled mesoporous SiO₂ matrices also prepared by a nanocasting strategy. While systems (i) and (ii) are appealing from a magnetic viewpoint, system (iii) shows interesting and novel optical properties.

2. Enhanced magnetic properties in hard ferromagnetic particles embedded in an oxide matrix

The large variety of ferromagnetic materials that exist in nature can be roughly classified into two categories: soft and hard ferromagnetic materials. Soft ferromagnetic materials are characterized by low values of coercivity, H_C , typically lower than 10 Oe, and large values of saturation magnetization, M_S , usually higher than 100 emu/g. This results in narrow hysteresis loops [see Figure 1(a)]. Some examples of soft FM materials are Fe, Ni, permalloy or FeSi alloys. They are used in, for example, electromagnets or transformers cores. On the contrary, hard FM materials, which are also known as *permanent magnets*, are characterized by high values of H_C , typically larger than 500 Oe, and usually smaller values of M_S than soft magnetic materials, i.e. wide hysteresis loops [see Figure 1 (b)]. Some examples of hard FM are SmCo₅, Al-Ni-Co alloys or Nd₂Fe₁₄B. Permanent magnets have lots of applications in industry: in motors and generators, telecommunications (headphones, magnetic sensors, high-density magnetic recording media, ...), in synchrotrons (as systems for particles guidance), etc. (Hadjipanayis, 1999).



Fig. 1. Hysteresis loops of (a) a soft magnetic material and (b) a hard magnetic material.

The figure of merit of a hard magnetic material is its *energy product*, which is denoted by $(BH)_{Max}$, and is roughly proportional to the total area enclosed by the hysteresis loop. The values of $(BH)_{Max}$ give a good estimation of the quality of the hard magnetic material, since it is closely related to the overall energy that can be stored in the magnet. Obviously, magnets with higher $(BH)_{Max}$, would require smaller sizes to have the same efficiency. In order to maximize $(BH)_{Max}$ it is necessary to have a large H_C, high values of M_S and a squareness ratio, M_R/M_S (where M_R is the remanent magnetization), as close to 1 as possible. The result of increasing H_C

is a widening of the hysteresis loop, while increasing M_S results in a lengthening of the loop along the magnetization axis. Finally, an increase of M_R/M_S makes the loop squarer. The net effect in all three cases is an enhancement of the energy product. Figure 2 shows a historical evolution of the maximum energy product, (BH)_{Max}, that has been accomplished during the last century in different types of hard FM materials.



Fig. 2. Chronological evolution of the energy product values, at room temperature, in permanent magnetic materials during the last decades.

Permanent magnet development has been traditionally based on the search for materials with a large magnetocrystalline anisotropy and/or reduction of the particle size to obtain isolated single-domain particles (Hadjipanayis, 1999). In recent years, processing of hard and soft magnetic composites (termed spring magnets) has also been used to improve permanent magnet properties. Exchange interactions between hard and soft grains bring about an increase of the saturation magnetization (M_S) of the composites. This increase of M_S , despite of the reduction of the coercivity (H_C), produces an increase of their energy product, (BH)_{Max}, of the magnet (Kneller & Hawig, 1991). In this work, we demonstrate that similar to what is observed in thin film systems (Nogués & Shculler, 1999), inducing an exchange interaction between FM and AFM powder materials results in an enhancement of both H_C and the M_R/M_S ratio of the hard magnet.

In our case, the coupling is accomplished by a mechanical grinding process of the FM (SmCo₅) and AFM (NiO) components. As in spring magnets, under suitable conditions an increase of the (BH)_{Max} of the FM can also be achieved (Sort et al., 2002). A typical scanning electron microscopy image, corresponding to SmCo₅ particles embedded in a NiO matrix (in a weight ratio 1:1) is shown in Figure 3.

Typically, a cooling treatment under a magnetic field from above the Néel temperature of the AFM phase is required in order to induce FM-AFM exchange interactions. In our case, no heating/cooling was purposely performed on the as-milled powders. However, it is well-known that, due to the impacts between the powder and balls, temperature can locally rise significantly during the milling, eventually exceeding the Néel (or blocking)



Fig. 3. Scanning electron microscopy image of $SmCo_5$ particles (light) embedded in a NiO matrix (grey). The image corresponds to $SmCo_5$ milled with NiO, for 32 h, in a weight ratio 1:1.

temperature of the system (Murty & Ranganathan, 1998). As a result, and due to the stray fields emanated from $SmCo_5$ grains, an exchange interaction is likely to be set during the milling of this composite material due to an instantaneous heating/cooling process caused by the above mentioned impacts. Consequently, the spins of the AFM grains located near the interfaces with the FM particles will tend to align towards the directions of the neighbouring FM domains (see Figure 4). During magnetic field switching, the FM-AFM coupled grains will tend to reverse together but since they are exchange-coupled the coercivity will increase.

As milling proceeds, the crystallite sizes of the different phases which form the composite material (i.e., SmCo₅ and NiO) progressively decrease. The obtained values of coercivity are particularly large for intermediate SmCo₅ crystallite sizes and larger AFM weight fractions (see Figure 5).

Actually, several factors have to be taken into account in order to explain the milling time dependence of H_C in ball milled $SmCo_5$ and $SmCo_5 + NiO$ powders. As shown in Figure 5, H_C increases for short milling times in $SmCo_5$ either when it is milled alone or with NiO. This can be mainly attributed to the particle size reduction associated with the milling process. Indeed, the unmilled $SmCo_5$ particles are several μ m in size. Therefore, they are mainly in a multidomain state. However, as the milling time increases, the FM particles fracture and become smaller. Thus, many of them reach sizes of around 1 μ m (see Figure 3). Therefore, after intermediate milling times, a fraction of $SmCo_5$ particles may be in a monodomain state. This can be the reason for the increase of H_C during the first stages of the mechanical milling process, although small defects acting as pinning sites could also play some role. However, for long enough milling times H_C is found to significantly reduce. We have attributed this reduction to the high degree of structural disorder generated in $SmCo_5$ after long-term milling, which results in a decrease of its magnetic anisotropy and, thus, of its coercivity (Strnat & Strnat, 1991; Leslie-Pelecky & Schalek, 1999).


Fig. 4. Intuitive illustration of the morphology and spin configuration of $SmCo_5 + NiO$ powders ball milled together. In (a) the morphology after short-term milling is illustrated, i.e. the FM and AFM particles are still not soldered together. In particular, one FM and two AFM particles are represented, each of them containing a few magnetic domains, which, at the same time, include several crystallites. Note that in (a) the spins in the FM and the AFM do not interact with each other and, consequently, the magnetization directions in the different domains are at random. Panel (b) represents the morphology generated after long-term milling. In this case, two FM particles have soldered with AFM powders to form one FM-AFM agglomerate. For simplicity, only the crystallites in the AFM located at the interfaces with the FM particles have been represented. The figure shows that, if one assumes that some FM-AFM exchange interactions are induced during the milling, the spins of the AFM grains located near the interfaces with the FM particles will tend to align towards the directions of the neighboring FM domains. This coupling at the interface will result in the local exchange bias effects, i.e. an enhancement of coercivity.



Fig. 5. Dependence of the coercivity, H_C , on the SmCo₅ crystallite size (which is, in turn, tuned by varying the milling time) for SmCo₅:NiO milled in a weight ratio of 1:0 (- \Box -), 3:1 (- \bullet -), 3:2 (- \bullet -) and 1:1 (- \star -). The lines are a guide to the eye.

The increase of H_C with the NiO content is due to an enhancement of FM-AFM exchange interactions. In order to verify the role of NiO in this H_C increase, ball milling of SmCo₅ was also performed with CoO (which is paramagnetic at room temperature). As shown in Figure 6, the structural refinement of SmCo₅ crystallite size during ball milling is similar than for NiO (values as small as 10 nm are obtained after long-term milling, e.g. 32 h). It can be seen that, in the three cases, the maximum H_C is obtained for $\langle D \rangle_{SmCo5}$ of the order of 10-15 nm. Moreover, Figure 6 also shows that for a fixed crystallite size, H_C remains higher in SmCo₅ + CoO than for SmCo₅ milled alone. This behavior can be understood in terms of the role that the paramagnetic CoO matrix plays in isolating the different SmCo₅ grains. This isolation brings about a decrease of the interparticle FM-FM exchange interactions, which are known to reduce H_C due to the cooperative reversal of several interacting FM particles (Schrefl et al., 1994). Nevertheless, the fact that, for a fixed SmCo₅ crystallite size, H_C is even higher when it is milled with NiO can be taken as a confirmation that FM-AFM exchange interactions are actually present in the as-milled SmCo₅ + NiO powders.

In spite of the coercivity enhancement, the presence of NiO inevitably results in a reduction of the overall saturation magnetization of the composite (due to the zero net magnetization of the AFM phase), which is again proportional to the NiO content. Hence, $(BH)_{Max}$ is reduced when the NiO content is increasingly high, as for example in the case of the 1:1 ratio (see Figure 7). Nevertheless, due to the coercivity increase associated with the FM-AFM coupling, $(BH)_{Max}$ in 3:1 SmCo₅:NiO (with SmCo₅ crystallite size around 15 nm, corresponding to a milling time of 4 h) is enhanced with respect to SmCo₅ alone.



Fig. 6. Dependence of the coercivity, H_C , on $SmCo_5$ crystallite size, $\langle D \rangle_{SmCo_5}$, for $SmCo_5$ milled alone (————), with CoO (———) and NiO (——O—) in the weight ratio 1:1. The lines are a guide to the eye.



Fig. 7. Dependence of the energy product, $(BH)_{Max}$, on the SmCo₅ crystallite size (which is, in turn, tuned by varying the milling time) for SmCo₅:NiO milled in a weight ratio of 1:0 (- \Box -), 3:1 (- Φ -), 3:2 (-A-) and 1:1 (- \star -). The lines are a guide to the eye.

It is noteworthy that, due to the interplay of all the different effects, the enhancement of $(BH)_{Max}$ in this class of materials needs optimization of both the milling time and the FM:AFM weight ratio. Figure 8 summarizes the maximum values of H_C and $(BH)_{Max}$ that can be achieved in SmCo₅-NiO composite materials after proper optimization of the milling time and FM:AFM weight percentage.



Fig. 8. Dependence of the maximum achievable values of coercivity, H_{C} , and energy product, $(BH)_{Max}$, as a function of the SmCo₅ weight percentage. The values plotted correspond to the milling times that give maximum H_{C} and $(BH)_{Max}$ for each composition.

3. Tunable magnetic behaviour in oxide-oxide composite materials synthesized by nanocasting approach

Unlike ball-milling, which is a quite unique top-down approach for the synthesis of nanostructured composite materials, other approaches such as the template-assisted methods based on a bottom-up strategy are also currently receiving a great deal of attention. Among them, the multi-step nanocasting method is based on the confined growth of transition metal oxides, metals and metal chalcogenides within the pores of ordered inorganic matrices (Lu et al., 2010). Mesoporous silicas, which are characterized by ordered arrays of porous with diameters in the range between 2 nm and 50 nm, are the key materials in the field of 'host-guest chemistry'.

Since the first mesoporous silica material, MCM-41, was discovered by scientists of the Mobil Corporation in 1992 (Beck et al., 1992), several mesoporous silica structures have been developed (e.g. SBA-15, KIT-6, SBA-16, FDU-1, to name a few). The main difference between these silica structures relies on pore topology. While SBA-15 and KIT-6 feature channel-type

mesopores accessible from outside, SBA-16 and FDU-1 consist of much less accessible cagelike cavities interconnected by narrow throats. Typically, the silica hosts, which are themselves prepared by templating procedures, are impregnated with suitable precursors. When the confined growth of a transition metal oxide is pursued, the precursor is usually a nitrate salt. Among the impregnation procedures available, the so-called evaporation, solidliquid and two-solvent methods are the most employed so far. The precursor:silica molar ratio as well as the number of impregnation steps must be carefully controlled in order to maximize the filling of the silica host while avoiding the growth of non-mesoporous particles outside the mesoporous silica structure. The impregnated silicas are then calcined in atmospheric conditions to convert the nitrate salt into the corresponding oxide, thereby yielding a SiO₂@Me_xO_y (Me = metal) nanocomposite (Figure 9). Further etching of the SiO₂ matrix can be done with diluted NaOH or HF solutions to obtain the Me_xO_y as negative replica of the SiO₂ host.



Fig. 9. Sketch of nanocasting pathway for the synthesis of $SiO_2@Me_xO_y$ nanocomposites. Further selective etching of the SiO_2 matrix releases the Me_xO_y as a negative replica of the SiO_2 host.

Figure 10 shows transmission electron microscopy (TEM) images of SBA-15 SiO₂ and of $SiO_2@Co_3O_4$ composite synthesized using the former as a host. The SBA-15 silica consists of a well-ordered hexagonal array of one-dimensional channels, whose diameter can be typically varied in the range of 6–15 nm depending on the synthesis conditions. Here, impregnation of the silica host (pore size around 7 nm) with the metal oxide precursor was carried out by evaporation: the silica powder was suspended in ethanol and put in contact

with a given amount of cobalt nitrate salt, stirred for 24 h and left for ethanol evaporation. Then, a calcination at 550° C made it possible to convert the precursor into AFM Co₃O₄, whose growth took place inside the silica channels. The darker areas in the TEM image correspond to the Co₃O₄ material confined within the silica mesopores. A similar procedure was carried out taking AFM NiO and ferrimagnetic (FiM) NiCo₂O₄ spinel as guest materials. It is noteworthy that these oxides are highly crystalline. This is related to the excellent thermal stability of the silica skeleton, which allows a relatively high calcination temperature. In contrast, for sol-gel or soft-templating approaches, the heating temperatures are much more restrictive.



Fig. 10. TEM images of (a) SBA-15 SiO₂ template and (b) Co₃O₄-filled SBA-15 SiO₂.

As mentioned before, release of the guest material confined within the silica channels is feasible using diluted NaOH or HF solutions to selectively etch the silica host, leading to transition metal oxides displaying ordered arrangements of mesopores with high surface areas. To date, most of the works concerning the synthesis of mesorelief metal oxides rely on single metal oxides (e.g WO₃, In₂O₃, CeO₂, Co₃O₄, NiO, Fe₃O₄) (Tiemann, 2008). Application of these materials in many different fields like heterogeneous catalysis, gas-sensing, optics, etc. has been already demonstrated but there is still room to explore new functionalities, in particular from the magnetic perspective. In this sense, we have tackled the synthesis of compositionally graded oxide-oxide composites, namely NiO/NiCo₂O₄/Co₃O₄, via replication of SBA-15 silica template. For this purpose, the SBA-15 silica host was impregnated with nickel and cobalt nitrate salts in different Ni(II):Co(II) molar ratios following the evaporation method above described. The impregnated silica was then calcined at 550°C and the SiO₂ template further removed. Selective etching of the SiO2 host was carried out in diluted NaOH solution under stirring for 24 h. The NiO/NiCo₂O₄/Co₃O₄ nanocomposite powders were collected after centrifugation and decanted off the supernatant, thoroughly rinsed in ethanol and finally dried in vacuum. Depending on the nominal Ni(II):Co(II) molar ratio, either NiO-rich or NiCo₂O₄-rich nanocomposites can be obtained. From the morphology viewpoint, hexagonallyarranged cylindrical nanowires were obtained for high Co(II):Ni(II) molar ratios, whilst randomly organized rods were obtained for low Co(II):Ni(II) ratios. The diameter of these nanorods/nanowires is around 8 nm (or slightly less), which correlates nicely with the pore size of the parent SBA-15 silica owing to the confined growth of the solid within the silica channels. Also, the composites are highly crystalline as demonstrated by high-resolution TEM images and X-ray diffraction patterns (not shown).

The distinct magnetic character of the constituent phases (NiCo₂O₄ is FiM while NiO and Co₃O₄ are AFM) allows to properly tune the magnetic behaviour of the final composite (Cabo et al., 2010). Figure 11 shows the dependence of the saturation magnetization, M_S , of these hybrid materials as a function of the NiCo₂O₄ amount. The M_S values were extracted from the corresponding hysteresis loops at 10K after substracting the linear contribution. It is noteworthy that the magnetization did not saturate at the maximum applied field of 70 kOe due to the presence of the AFM phases (NiO and Co₃O₄) and magnetic disorder effects usually observed at the nanoscale (Batlle & Labarta, 2002). Although M_S depends linearly on the amount of NiCo₂O₄, the coercivity varies non-monotonically, giving rise to values between 170 Oe and 1600 Oe, caused mainly by the AFM-FiM coupling (Nogués & Schuller, 1999) of the composites.

Significantly, the rich-NiCo₂O₄ composites are still FiM at room temperature, which means that the superparamagnetic blocking temperature, T_B , is above 300 K. Such enhanced T_B may arise from an increase of the effective anisotropy due to the shape anisotropy and the FiM-AFM exchange coupling. This makes it possible to foresee innovative applications for these nanocomposites since the powders could be trapped or guided to specific locations by using small magnetic fields. Such attribute could be exploited, for instance, in magnetic hyperthermia applications.



Fig. 11. Saturation magnetization (\blacktriangle) and coercivity (\Box) (at T = 10 K) dependence of the nanocomposites with the amount of FiM NiCo₂O₄. The amount of NiCo₂O₄ was estimated by Rietveld refinement of the corresponding X-ray diffraction patterns. The dashed line is an eye-guide.

Although the replication process entailed the loss of some mesostructural order, the Brunauer-Emmett-Teller (BET) area of the composites is in the range of 60-80 m²/g, which can be considered as moderately large. Hence, these materials benefit from reasonably high surface areas and tunable magnetic properties. Remarkably, other silica mesostructures can be used to obtain mesorelief oxide-oxide nanocomposites. As an example, we show a TEM image of a NiCo₂O₄-NiO nanocomposite obtained using SiO₂ KIT-6 as a template [Fig. 12(a)] together with its corresponding magnetic hyteresis loop [Fig. 12(b)]. Unlike the SBA-15 silica, the KIT-6 one displays a gyroidal structure characterized by a 3D interpenetrating network of channels. The corresponding replicas typically feature hexagonal rings like the one shown in Figure 12(a).



Fig. 12. (a) TEM image of a KIT-6 templated NiCo₂O₄-NiO (7 wt% NiO) composite (notice the hexagonal rings typical of this mesostructure) and (b) its corresponding hysteresis loop at 10 K.

4. Novel optical properties in semiconductor materials confined in mesoporous silica matrices

If the confined material within the silica channels is not a metal oxide but a metal chalcogenide, that is, a II–VI semiconductor like CdSe, CdTe or CdS, then the optical properties of the resulting composite can be exploited (Li et al., 2008). The synthesis of II–VI semiconductor nanocrystals has been extensively investigated both from fundamental and applied standpoints due to their luminosity, nonlinear optical properties and quantum effects, making them excellent for applications in electrical, photoelectrical and biologic devices. Compared to the case of transition metal oxides, the confined growth of metal chalcogenides within silica templates has been much less explored, mainly because of the need of non-commercial, hybrid precursors able to render the metal calchogenide at temperatures well below the formation of cadmium oxide. For this reason, instead of using a single-source precursor, other strategies like the Cd^{2+} ion exchange reaction in the inner pores of mesoporous silica during a treatment with H₂S gas have also been attempted (Wang et al., 2002).

Here we show that the photoluminescence properties of CdS nanocrystals embedded in silica matrices and derived from a single-source precursor differ from the behavior displayed by the mesorelief nanocrystals. Different silica mesostructures (i.e. SBA-16, KIT-6 and SBA-16) were impregnated with cadmium thioglycolate. The heat-treatment was carried out at low temperature in two stages (120 and 160°C) to render CdS. A TEM image of the SBA-15 SiO₂@CdS composite is shown in Figure 13(a), in which the location of the CdS can be identified by the darker regions. Figure 13(b) shows a HRTEM image of the highly-crystalline CdS replica obtained following template removal. The CdS replica is composed of nanocrystals arranged in the form of wires (an image at lower magnification is shown in the inset, where the SBA-15 mesostructure can be clearly identified).



Fig. 13. TEM image of (a) SBA-15 SiO₂@CdS composite and (b) *free* CdS nanocrystals in SBA-15 structure (a view at lower magnification is shown in the inset).

A comparison of the normalized photoluminescence (PL) spectra acquired at room temperature using a confocal laser scanning microscope (CLSM) in the 435 - 774 nm range for both samples is presented in Figure 14(a). The samples were excited at 405 nm (near-UV) laser wavelength. Compared to pure CdS replica, the emission band of the SBA-15 SiO₂@CdS composite broadens and its maximum is shifted to shorter wavelengths. Similar results were observed for KIT-6 SiO2@CdS composite when compared with its corresponsing CdS replica [Figure 14(b)]. The exact nature of the emission mechanism in semiconductor nanocrystallites is very complex and a clear picture has not yet emerged. Nevertheless, the photoluminescence arising from CdS nanoparticles is in general attributed to the surface defect emission and it is likely that the silica shell may influence it somehow. Figure 15 shows a comparison between the non-normalized PL spectra of SBA-16 SiO₂@CdS composite (i.e. a CdS-filled cage-like silica matrix) and the released CdS crystals after template removal. Notice the huge difference in intensity between both curves, especially bearing in mind that the SBA-16 SiO₂ matrix alone does not emit within the same wavelength range. It is therefore evident that the amorphous silica coverage of the CdS crystals enhances the PL response. Most importantly, because the CdS nanocrystals are embedded within the silica matrix, it effectively protects the CdS from undesirable photoinduced oxidation (Wei et al, 2008).



Fig. 14. Normalized PL spectra of (a) SBA-15 SiO₂@CdS composite (black curve) and *free* CdS nanocrystals (red curve), (b) KIT-6 SiO₂@CdS composite (black curve) and *free* CdS nanocrystals (red curve).



Fig. 15. Non-normalized PL spectra of SBA-16 $SiO_2@CdS$ composite (black curve) and *free* CdS nanocrystals (red curve). Notice the huge difference in intensity between both curves, especially taking into account that the SB6-16 SiO_2 host alone does not emit.

5. Conclusion

The transition from microstructured to nanostructured engineering materials has been the subject of widespread research over the last years since nanocrystalline materials (i.e., nanostructured) can exhibit superior properties than conventional ones (i.e., microstructured). In particular, metal-ceramic (cermet) nanocomposites open a broad range of possibilities, aimed at utilizing in a synergetic way both the nanostructuring effects and the unique properties offered by metals and ceramics. Our results demonstrate that SmCo₅ nanoparticles trapped in NiO matrix exhibit tuneable and enhanced magnetic properties mostly depending on the SmCo₅ crystallite size. On the other hand, fine-tuning of the magnetic response is also feasible in oxide-oxide nanocast materials by combining ferrimagnetic (NiCo₂O₄) and antiferromagnetic (NiO and Co₃O₄) oxides. Moreover, these multiphase oxides present additional advantages such as moderately large surface areas due to their porous character and long-range order provided by the parent templates. Finally, semiconductor-silica composites show interesting optical properties thanks to the interface interaction between the semiconductor compound (CdS) and the silica shell. Examples presented here definitely demonstrate that oxide-based nanocomposites are suitable candidates for a wide range of innovative engineering applications.

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Electromagnetic Characterization of Composite Materials and Microwave Absorbing Modeling

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1. Introduction

This book chapter is based on the experimental activities conducted mainly at Sapienza University of Rome: Astronautic, Electric and Energetic Engineering Department in collaboration with University of Maryland, Institute for Research in Electronics and Applied Physics (IREAP). A branch of scientific research about composite materials is focused on electromagnetic characterization and subsequent application of electric conductive polymers. The use of such structures is relevant in aerospace/aeronautics, for electromagnetic (EM) protection from natural phenomena (lightning), and intentional interference with radar absorbing materials (RAM), in nuclear physics for shields adopted in particle accelerators, and for nuclear EM pulses (NEMP) protection, in electromagnetic compatibility (EMC) for equipment-level shielding, high-intensity radiated fields (HIRF) protection, anechoic chambers (for the realizations of wedges and pyramidal arrays), and human exposure mitigation. In this chapter, composite reinforced by carbon nanostructured materials are considered, mainly because of their interesting electromagnetic characteristics, such as high electrical conductivity and excellent microwave absorption. Composite materials as well their absorption capability are analyzed and numerical design of wide frequency band microwave absorbing structures is presented and discussed in details. It is crucial to highlight the need of interdisciplinary research fields to go through nanomaterials: besides nanotechnology, also electromagnetic wave propagation theory, composite materials manufacturing techniques, evolutionary computation algorithms, and use those to design the "quasi perfect absorber" are strongly required. In particular, we propose an inhomogeneous multilayer absorber made of micrometric graphite (at different wt%), and nanometric carbon particles (SWCNTs, MWCNTs, CNFs, at different wt%). At the end, an improvement of the traditional absorbers has been achieved upon optimization through an in-house winning particle optimization (WPO) algorithm, this last appositely conceived for absorbers optimization. Main goal of the presented work is to optimize the absorbers achieving lower values (< -10 dB) of both reflection and transmission coefficients for angular apertures within 40° of the impinging plane wave (general far-field approximation of whatever active source). The developed evolutionary computation code is flexible in the selection of the algorithm parameters such as frequency band, incidence angular range, overall maximum multilayer thickness, composite material type of each layer, possibility to decide if the design optimization procedure must privilege thickness minimization and/or microwave absorption maximization during design.

With respect to the present literature, the developed method considers the absorption capability taking into account both the reflection and the transmission properties of the entire multilayer structure. Moreover the absorption properties of the multilayer structures have been analyzed considering oblique incidence at fixed angles within a finite range.

From the above explanation it is easy to understand the importance of numerical techniques such as evolutionary computation to design and optimize the absorber.

Absorber mathematical model described in this chapter have been experimentally validated in laboratory (www.saslab.eu) located in DIAEE at Sapienza University of Rome. At the end of chapter the experimental validation is discussed.

2. Composite materials manufacturing and carbon filler analysis

This section focuses on characterization of nanomaterials adopted to build the electrically conductive composite materials and in nanostructured composite materials manufacturing. In formulating an electrically conductive composite material, a polymer is combined with highly conductive rigid particles. Electrical conductivity is accomplished though a certain level of particle-to-particle contact or close proximity. It is difficult to draw definite conclusions about electrical conductivity since it depends also from electromagnetic solicitation type, i.e., DC or AC current and type of electromagnetic wave propagation i.e., direct contacts electrodes or plane wave incidence on the composite material, [D.Micheli et al.,2010], [Xingcun Colin Tong, 2009], [Z. Ounaiesa et al., 2003]. Many further factors can affect the conductive properties of the filler loaded composite, including filler type, loading level, particle distributions, size, and shape, intrinsic conductivity of filler, process condition plating, and compounding. However, the key factors are particle conductivity, loading level and particle shape. The filler concentration -- i.e., the filler in weight % w.r.t. the polymer -- or the volume loading level of the filler is relevant in the *percolation* regime of the composite -- i.e., the threshold at which the composite changes form an insulator to a conductor.

As the filler loading is increased further and reaches a critical point, the conductive particles contact one another, and a continuous network is established. The sudden and precipitous drop in resistivity is achieved through a generation of a continuous network, which is defined as percolation threshold [Weber, M, & Kamal., 1997]. Once achieved the percolation, a majority of the filler particles are in contact with at least two of their nearest neighbours, thereby forming a continuous chain or network. An electrical charge could then be diffused through the composite via this network without encountering the high-resistance polymer resin. Additional filler loading beyond the percolation threshold does not substantially reduce the resistivity of the composite [Sichel, 1982], the greater the aspect ratio of the particles, the smaller the loading level needed to reach the percolation threshold [D.Micheli et al.,2010]. In addition, the mixing process (dispersion) plays an important role in the percolation and conductivity of the conductive composite material. For instance, increasing

the mixing time and hence the specific energy provided during the mixing process, the homogeneity of the spatial distribution of the conductive particle in the matrix is improved and the errors in composite material dielectric permittivity computation at microwave frequencies are reduced. Composite materials considered in this work are based on epoxy matrix reinforced with several species of carbon nanomaterials. These latter have been chosen taking into account the lowest market prices: the economic aspects, normally neglected in small laboratory applications, are on the contrary important in real applications where the amount of carbon nanopowders fillers could be relatively high. In such scenario a good compromise in terms of cost/performances has been obtained using industrial grade multiwall carbon nanotubes (MWCNTs, about 300 \$/kg), graphite micropowder (about 40 \$/kg). Carbon nanofibers (CNFs, about 30 \$/g) has been mainly considered only in the carbon nanopowders analysis, while low cost MWCNTs and graphite micropowder have been largely adopted in the large multilayer tile manufacturing.

2.1 Carbon filler characterization

Carbon materials and epoxyresin considered in the experiments are:

- Micro Graphite (granular size < 20 μm), bought at SigmaAldrich;
- SWCNTs (Single Wall Carbon Nanotubes), bought at Carbolex (diameter around 1-2 nm, length 5-30 μm); http://www.nanotube-suppliers.com
- CNFs (Carbon NanoFibers), bought at SigmaAldrich (diameter around 75 nm, length 50-100 μm); http://www.sigmaaldrich.com/sigma-aldrich/home.html
- MWCNTs (Multi-Wall Carbon Nanotubes type NANOCYLTM NC7000), bought at NANOCYL (diameter around 9.5 nm, length 1.5 μm, purity 90%) http://www.nanocyl.com
- Epoxy-resin is: Prime™ 20LV(density 1.123 g/cm³), Hardner(density 0.936 g/cm³); http://www.gurit.com/

Carbon materials weight ratio (wt%) with respect to the polymer (epoxy-resin) are mainly in the range 0.5-3 wt%. Scanning electron microscope (SEM) analysis has been widely adopted in laboratory using VEGA TESCAN SEM model www.tescan.com. In particular, in Fig. 2.1.1, a), b) pictures of functionalized SWCNTs are shown. Functionalization is used to purify CNTs from impurities due to the manufacturing process of CNTs. This can be also carried out through microwave heating, mainly performed by an electromagnetic cavity where the field homogenization can be efficiently achieved [Prato et al., 2008]. In such a process, *a priori* evaluation of power absorption plays a crucial role in prediction of impurity densities. Comparing dimensions of SWCNTs and MWCNTs, it can be observed about 0.05 μ m for SWCNTs are typically 40 times greater then SWCNTs. Also topologies of CNTs network appear different: as a matter of fact MWCNTs are rope-like of bundled MWCNTs. Such agglomerations (joint twisting and wrapping) of MWCNTs constitute a trouble in composite materials manufacturing, because of intrinsic difficulties in dispersing CNTs within epoxy resin matrix – i.e., overcoming physico-chemical bonds.

The individual particles in fact are held together by attraction forces of various physical and chemical nature, including Van Der Waals forces and liquid surface tension. The attraction forces must be overcome in order to deagglomerate and disperse the particles into liquid

media. Sonication is a process where ultrasounds are used to drastically reduce the size of particle agglomerates melting against natural attraction forces. Ultrasonic cavitation generates high shear forces that break particle agglomerates into single dispersed particles.



Fig. 2.1.1 a) SWCNTs zoom 5x (10μm scale), b) SWCNTs zoom 30x (2μm scale), c) MWCNTs zoom 5x (10μm scale), d) MWCNTs zoom 15x (2μm scale),

In order to easily compare dimensions of different carbon powders, we report a some picture showing the typical carbon fiber (CF) and carbon nanomaterials we used as SWCNTs MWCNTs and carbon nanofiber (CNFs).

In polymerization process, epoxy-resin tend to spirally wrap CNTs, and if dense CNTs agglomeration takes place the polymerization process sometimes fails and localized parts of composite material could remain in a liquid status without completing the polymerization phase. Such structures are electromagnetically relevant themselves as they might exhibit planar chirality.

This is why we tried to break up MWCNTs by means of sonication.



Fig. 2.1.2. a) Carbon Fiber (CF) zoom 20x (2µm scale), b) Carbon Nanofiber (CNFs) zoom 20x (2µm scale), c) Multi Wall Carbon Nanotube (MWCNTs) zoom 20x (2µm scale), d) Single Wall Carbon Nanotube (SWCNTs) zoom 20x (2µm scale).

2.2 Nanostructured composite material manufactoring

Manufacturing of carbon based nanostrucutred composite materials is achieved through the following steps:

- Eventual carbon powders functionalization.
- Mixing, sonication and degassing of epoxy-resin and carbon nanopowders mixed dispersed with desired weigh percentage;
- Hardener adding, if required by the epoxy-resin;
- Composite curing by oven treatment.

First step is crucial in preparation of homogeneous composite materials. In Fig. 2.2.1, pictures of composite materials preparation are shown. Composite pictures before and a after sonication phase are shown.

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Fig. 2.2.1. a) Ingredients: Epoxyresin and MWCNTs, b) MWCNTs 3%wt and epoxy-resin manually mixed before sonication, c) Sonication process, d) MWCNTs 3%wt and epoxy-resin mixture after sonication.

Observing picture of same composite material before and after sonication phase, immediately appear the difference in the dispersion of MWCNTs.

Nanostructured composite material manufacturing process end up with the injection of described treated liquid mixture in the appropriate sample holder and curing with the appropriate oven treatment. In Fig. 2.2.2., sample holder and oven are shown. In our case, curing process requires about sixteen hours at temperature of 50 C°.

3. Nanostructured composite materials permittivity and microwave absorption characterization

3.1 Microwave measurements

In this section measurement of permittivity of nanostructured composite materials are shown. The microwave characterization process has been carried out by performing scattering parameter measurements and extracting the complex electrical permittivity through canonical algorithms. In particular, we performed the permittivity retrieval by using different algorithms and comparing produced results. The algorithms adopted are Nicholson-Ross, NIST iterative, and non-iterative [L. F.Chen & C. K. Ong, 2004], [Abdel-Hakim & Boughriet, 1997], [James Baker-Jarvis, 1990]. The so obtained results can be



Fig. 2.2.2. a) Injection of liquid composite materials into sample-holder; b) Oven treatment: 16 hours and 50 C°; c,d) Final sample within sample holders for wave guide measurement of electromagnetic properties of composite materials in the band 4-18 GHz; e,f) 200x200 mm tiles of composite materials for free space electromagnetic absorbing measurements.

considered accurate within the limit of the employed numerical methods. Microwave scattering parameters S_{ij} , with i,j = 1,2, [Davide M. Pozar, 2005], are measured using a Vector Network Analyzer (N5230C Agilent PNA-L) in the waveguide method shown in Fig.3.1.1. Wave guide calibration kit are in the J-band (5.38-8.18 GHz)), X-band (8.2-12.4 GHz), P-band (12.4-18 GHz). Sample holders, hosting the materials under test (MUT), were built using as a shape model the thru connections of Flann and Agilent calibration kits (www.flann.com, www.agilent.com).



Fig. 3.1.1. a,b,c) Waveguide sections and sample holders covering 5.3 to 18 GHz frequency band.

Scattering parameters connect the input and output circuit quantities using the reflection and transmission parameters normally adopted in microwave analysis. By means of such parameters it is possible to determine the real and the imaginary part of the electrical permittivity and magnetic permeability. All materials have some response to magnetic fields but, except for ferromagnetic and ferromagnetic types, their responses are usually very small, and their permeability values differ from μ_0 by a negligible fraction. In our experiment the relative magnetic permeability is that of free space ($\mu_r = 1$) since no ferromagnetic materials are involved.

The entire frequency-band has been divided in 1536 frequency steps (start 5.38 GHz, end 18 GHz) and, for each one, the corresponding electrical permittivity has been computed. Composite materials based on different weight percentage of carbon nanopowders with respect to the epoxyresin have been analyzed. In particular 0.5, 1, 2, 2.5, 3 % wt for MWCNTs based composite materials and 1, 2, 3wt.% for CNFs based composite materials.

Observing Fig.3.1.2, it can be noticed that the higher the filler weight percentage, the greater both the real and imaginary part of permittivity. This can be ascribed to the electric conductive characteristic of the carbon powders inserted into the epoxy matrix [D.Micheli et al., 2010].

In the next section the analysis of materials in terms of electric losses is made.

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Fig. 3.1.2. a) Real component; b) Imaginary component of permittivity of nanostructured composite materials based on MWCNTs; c) Real component; b) Imaginary component of permittivity of nanostructured composite materials based on CNFs in the 5.3 to 18 GHz frequency band.

3.2 Microwave electric conductivity

Microwave electrical conductivity of a dielectric material can be evaluated by using the following equation:

$$\varepsilon_r'' = \frac{\sigma}{\omega \varepsilon_0} = \frac{\sigma}{2\pi f \varepsilon_0} \implies \sigma(S/m) = 2\pi f \varepsilon_0 \varepsilon''$$
(3.2.1)

Where σ is the electric conductivity (S/m), ε_0 is the free space permittivity (8.854 × 1E-12 F/m), *f* is the frequency (Hz), ε'' is the imaginary component of permittivity.

In Fig. 3.2.1, electric conductivity of nanostructured composite materials is reported as function of frequency.

In general, the electric conductivity of nanopowder reinforced composite materials is mainly due to a couple of effects: the first is the high number of inter-nanostructure connections which plays a role in ohmic resistivity reduction, the second is explainable by thinking to the reinforced matrix as a nanocapacitance network, where a single capacitor is constituted by two faced nanoparticles. The former effect is trivially related to the concentration, and becomes dominant above the percolation threshold, when many conduction pathways cross the matrix thus forming electrical connections. The latter is to be ascribed to the very large nanoparticles specific surface area (A) compared to micro-sized powder: the resulting effective capacitance (C) lowers the composite characteristic impedance, as clear from the fundamental capacitance impedance equation,

$$Z_c = \frac{1}{j\omega C} \tag{3.2.2}$$

(where $C \propto A$).



Fig. 3.2.2. a) Electric Conductivity (S/m) of MWCNTs based composite materials; b) Electric Conductivity (S/m) of CNFs based composite materials.

3.3 Microwave absorption properties related to impedance matching conditions

From permittivity results, the intrinsic wave impedances of the k-th material can be computed using the following equation.

$$\eta_{k} = \sqrt{\frac{\mu_{0}}{\varepsilon_{0}}} \sqrt{\frac{\mu_{rk}}{\varepsilon_{rk}}} = \sqrt{\frac{\mu_{0}}{\varepsilon_{0}}} \sqrt{\frac{\mu_{rk}}{\varepsilon_{rk}' - j\varepsilon_{rk}''}}$$
(3.3.1)

Where μ_{rk} is the relative permeability of the composite (equal to 1), ε_{rk} is the relative permittivity of the composite which is function of the frequency. Intrinsic wave impedance is a complex number and magnitudes are reported in Fig. 3.3.1.

Observing the intrinsic wave impedance plot, it is possible to note that the higher the weight concentration of carbon nanopowders, the lower the intrinsic wave impedance of composite material. As shown in [D.Micheli et al.,2010], the wave impedance plays an important role in microwave reflection and absorption properties of materials in free space propagation condition, in the next section absorbing effectiveness of materials is described.

There are three conditions that can minimize the EMI reflection from a surface. When an electromagnetic wave, propagating through a free space with impedance of Z_{0} , happens upon a semi-infinite dielectric material boundary of impedance Z_i , a partial reflection



Fig. 3.3.1. a) Intrinsic wave impedance of nanostructured composite materials based on MWCNTs in the 5.3 to 18 GHz frequency band; b) Intrinsic wave impedance of nanostructured composite materials based on CNFs in the 5.3 to 18 GHz frequency band

occurs. The reflection coefficient (dB), at the interface can be expressed using formalism of transmission lines [S. Ramo, J. Whinnery & T. Van Duzer, 1994]:

$$RC(f) = 20Log_{10} \left| \frac{(Z_i - Z_0)}{Z_i + Z_0} \right|$$
 (3.3.2)

Where:

RC = Reflection Coefficient (dB);

 $Z_0 \sim 377$ (Ω) is the free space impedance;

Z_i=Input impedance at the Air-Absorber interface;

f =frequency (Hz).

The reflection coefficient falls to $-\infty$ when $Z_i=Z_0$, or, in other words, the composite material layer is impedance matched to the incident medium.

Therefore, the absorbing material must be lossy (second condition), so that the EMI energy can be dissipated within the material and impedance matched (first condition), so that the electromagnetic wave is not reflected back. But in order to get a large amount of attenuation, values of permeability and/or permittivity should be large; this condition could imply low values of intrinsic impedance and as a consequence large values of RC(dB). As a consequence design of an absorber is a compromise between the front-face reflection coefficient and the loss per unit thickness. One method to search for the best compromise within the largest frequency band is the multilayer structure. Here the optimization of material of each layer and its related thickness play an important role in absorption maximization.

Some of these structures are characterized by a surface impedance Zi, close as possible to free-space impedance ($\sim 377\Omega$), and then changing their intrinsic impedance inside by gradually increasing their conductivity to keep the reflection coefficient at the boundary of each layer as low as possible, and allow the materials to convert the EMI energy into Joule heating for dissipating. There are a variety of absorbers but they can be classified into two basic types of structures and materials: resonant or graded dielectric or both of them.

In the next section a new search algorithms and absorbers design method are deeply analyzed. The third condition to obtain an absorber can be easily understood rewriting equation of reflection coefficient:

$$RC(f) = 20Log_{10} \left| \frac{(Z_i - Z_0)}{Z_i + Z_0} \right| = 20Log_{10} \left| \frac{\left(\frac{Z_i}{Z_0} - 1\right)}{\left(\frac{Z_i}{Z_0} + 1\right)} \right|$$
(3.3.3)

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$$if \quad \mu_{rk} = \varepsilon_{rk} \quad \Rightarrow \quad \frac{Z_i}{Z_0} = \frac{\sqrt{\frac{\mu_0}{\varepsilon_0}}\sqrt{\frac{\mu_{rk}}{\varepsilon_{rk}}}}{\sqrt{\frac{\mu_0}{\varepsilon_0}}} = \sqrt{\frac{\mu_{rk}}{\varepsilon_{rk}}} = 1 \quad \Rightarrow \quad RC(dB) \to -\infty$$
(3.3.4)

In other words when relative permittivity is close to relative permeability values then, the material intrinsic impedance become close to free space impedance (377 Ω) and reflection of electromagnetic wave become very low.

4. Numerical design and optimization of microwave absorber

4.1 Introduction

This Section describes the approach adopted to design and optimize the microwave absorber multilayer structure. First the design and optimization problem are introduced and the electromagnetic model of absorber is described, then, winning particle optimization (WPO) method, are analyzed and applied for the numerical design of the microwave absorber.

Two kind of structures are designed, one explicitly required in microwave absorbing materials (MAM), the other in microwave shielding structures (MSS).

The first commonly called radar absorbing materials (RAM) are mostly known for their applications in stealth fighters and anechoic chambers; the second is developed for enhanced shielding applications where requirements are simultaneously both: microwave shielding and microwave absorbing capability of materials.

Electromagnetic Interference (EMI), defined by NATO as an electromagnetic disturbance which interrupts, obstructs, or otherwise degrades the effective performance of electronic or electrical equipment. In aircraft, EMI can affect everything from fly-by-wire flight control systems to a cockpit fuel gauge and in extreme cases put a plane into an uncommanded dive or shut down a critical avionic system.

Naturally occurring radio noise originating from atmospheric disturbances (including lightning) and extraterrestrial sources (such as sunspots) can also degrade the performance of electronic equipment. Communications signals may also interfere with the operation of sensitive electronic equipment. The most common type of EMI occurs in the radio frequency (RF) range of the electromagnetic (EM) spectrum, from 10⁴ to 10¹² Hertz. This energy can be radiated by computer circuits, radio transmitters, fluorescent lamps, electric motors, overhead power lines, lightning, and many other sources, and device failures caused by interference—or "noise"—from electromagnetic energy are increasing due to the growing number of products that contain sensitive electronic components. This is why we are

studying structures which simultaneously are able of absorbing and shielding from microwave point of view.

4.2 Electromagnetic model of multilayer absorber

In RAM applications, reflection coefficient (RC) at the first air-multilayer interface can been used as the main objective function (OF) parameter which need to be reduced using numerical optimization techniques, whereas in shielding ones the most stringent requirement considered is the transmission coefficient (TC) lowering. The multilayer absorption is a key feature in shielding applications too, because of evident protection constraints, so it has been quantified through the so-called 'loss factor' (LF%), defined as [D.Micheli et, al., 2009], and [D.M.Pozar, 2005]:

$$LF\% = \left(1 - |RC|^2 - |TC|^2\right) \cdot 100 \tag{4.2.1}$$

Where:

RC is the Reflection Coefficient expressed in the linear form.

TC is the Transmission Coefficient expressed in the linear form.

Its physical meaning is related to the fraction of the incident power vanishing inside the materials due to localization and dissipation phenomena. Since the calculation of RC and TC becomes a crucial point for the optimization goal, a rigorous approach to relate transmitted and reflected waves to the incident one inside each layer has been adopted. In particular, such theoretical model relies on the forward/backward propagation matrix formalism introduced in chapter one, accounting for each single interface effect on the local field crossing. Both normal and oblique incidences have been evaluated during the automatic optimization. Numerical optimization require the definition of some boundary conditions for the dimensions of the multilayer structure adopted as absorber model [D.Micheli et, al, 2010]. For all absorber presented in this book the thickness of each layer can range from 0 up to 3 mm. Number of layers of absorber is upper-limited to maximum ten layers. The effective number of layers is established each time by the numerical optimization procedure which is able to remove one or more layers of the multilayer structure. Multilayer configuration structures are depicted in Fig. 4.2.1.

It could be noticed that last layer could be air (i.e. free space in this context), or a perfect electric conductor (PEC) as a function of the absorber we are interested to optimize. Usually in typically RAM application PEC is applied since is assumed that such absorber need to be applied like a coating on an existing metal based structure like an airplane or a boat. On the contrary, in shielding application air is usually assumed as the surrounding medium for the absorber.

The design algorithm needs to be capable not only to choose the number of layers and their thickness but the material type too. In other words in the multilayer structure, layers order is not a priori fixed but numerical techniques decides completely all layers parameters, from layers number and layer thicknesses up to best composite material which must be adopted for each layer of the multilayer structure. Without lack of generality, the case of normal incidence is here reported, even though the current implemented formulation takes account of both TM/TE modes. For an arbitrary layer u of the configuration depicted in Fig.4.2.1 it is possible to write [D.Micheli et, al, 2010],



Fig. 4.2.1. General Multilayer scheme.

$$E_{u}^{+}e^{-j\kappa_{uz}z_{u}} + E_{u}^{-}e^{j\kappa_{uz}z_{u}} = E_{u-1}^{+}e^{-j\kappa_{u-1}z_{u}} + E_{u-1}^{-}e^{j\kappa_{(u-1)z}z_{u}}$$

$$\frac{\eta_{u+1}}{\eta_{u}}E_{u}^{+}e^{-j\kappa_{uz}z_{u}} - \frac{\eta_{u+1}}{\eta_{u}}E_{u}^{-}e^{j\kappa_{uz}z_{u}} = E_{u-1}^{+}e^{-j\kappa_{(u-1)z}z_{u}} - E_{u-1}^{-}e^{j\kappa_{(u-1)z}z_{u}}$$
(4.2.1)

now, summing and subtracting each member of Eq. (4.2.1), it is straightforward to obtain

$$\begin{pmatrix} 1 + \frac{\eta_{u-1}}{\eta_u} \end{pmatrix} E_u^+ e^{-j\kappa_{uz}z_u} + \begin{pmatrix} 1 - \frac{\eta_{u-1}}{\eta_u} \end{pmatrix} E_u^- e^{j\kappa_{uz}z_u} = 2E_{u-1}^+ e^{-j\kappa_{(u-1)z}z_u} \\ \begin{pmatrix} 1 - \frac{\eta_{u-1}}{\eta_u} \end{pmatrix} E_u^+ e^{-j\kappa_{uz}z_u} + \begin{pmatrix} 1 + \frac{\eta_{u-1}}{\eta_u} \end{pmatrix} E_u^- e^{j\kappa_{uz}z_u} = 2E_{u-1}^- e^{j\kappa_{(u-1)z}z_u}$$

$$(4.2.2)$$

In order to establish a clear relationship between fields in *u*-th and (*u*-1)-th layers, upon multiplication of $e^{-j\kappa_{u-1}(z_{u-1}-z_u)}$ by the first of (4.2.1), and by the second of (4.2.1), we obtain

$$\frac{1}{2} \left(1 + \frac{\eta_{u-1}}{\eta_u} \right) E_u^+ e^{-jk_{uz} z_u} e^{-jk_{(u-1)z} (z_{u-1} - z_u)} + \frac{1}{2} \left(1 - \frac{\eta_{u-1}}{\eta_u} \right) E_u^- e^{+jk_{uz} z_u} e^{-jk_{(u-1)z} (z_{u-1} - z_u)} = (4.2.3)$$

$$= E_{u-1}^+ e^{-jk_{(u-1)z} z_{u-1}}$$

$$\frac{1}{2} \left(1 - \frac{\eta_{u-1}}{\eta_u} \right) E_u^+ e^{-jk_u z_u} e^{+jk_{(u-1)z} (z_{u-1} - z_u)} + \frac{1}{2} \left(1 + \frac{\eta_{u-1}}{\eta_u} \right) E_u^- e^{+jk_u z_u} e^{+jk_{(u-1)z} (z_{u-1} - z_u)} = (4.2.4)$$

$$= E_{u-1}^- e^{+jk_{(u-1)z} z_{u-1}}$$

Then, considering field and propagator products with common subscripts and taking advantage of the matrix formalism, one gets

$$\begin{bmatrix} E_{u-1}^{+}e^{-jk_{(u-1)z}z_{u-1}}\\ E_{u-1}^{-}e^{+jk_{(u-1)z}z_{u-1}} \end{bmatrix} = \overline{V_{(u-1),u}} \cdot \begin{bmatrix} E_{u}^{+}e^{-jk_{uz}z_{u}}\\ E_{u}^{-}e^{+jk_{uz}z_{u}} \end{bmatrix}$$
(4.2.5)

Where:
$$R_{(u-1),u} = \frac{\left(1 - \frac{\eta_{u-1}}{\eta_u}\right)}{\left(1 + \frac{\eta_{u-1}}{\eta_u}\right)} = \frac{\eta_u - \eta_{u-1}}{\eta_u + \eta_{u-1}}$$
 (4.2.6)

$$\overline{V_{(u-1),u}} = \frac{1}{2} \left(1 + \frac{\eta_{u-1}}{\eta_u} \right) \left[\begin{array}{c} e^{-jk_{(u-1)z}(z_{u-1}-z_u)} & R_{(u-1),u}e^{-jk_{(u-1)z}(z_{u-1}-z_u)} \\ R_{(u-1),u}e^{+jk_{(u-1)z}(z_{u-1}-z_u)} & e^{+jk_{(u-1)z}(z_{u-1}-z_u)} \end{array} \right] = \\
\text{And:} = T_u^{-1} \left[\begin{array}{c} e^{-jk_{(u-1)z}(z_{u-1}-z_u)} & R_{(u-1),u}e^{-jk_{(u-1)z}(z_{u-1}-z_u)} \\ R_{(u-1),u}e^{+jk_{(u-1)z}(z_{u-1}-z_u)} & e^{+jk_{(u-1)z}(z_{u-1}-z_u)} \end{array} \right] = \\$$
(4.2.7)

In (4.2.5) the 'local' transmission coefficient takes the usual form

$$T_u = \frac{2\eta_u}{\eta_u + \eta_{u-1}}$$
(4.2.8)

as well as the 'local' reflection coefficient:

$$R_{u-1} = \frac{\eta_{u-1} - \eta_u}{\eta_{u-1} + \eta_u} \tag{4.2.9}$$

Both the expressions involve the intrinsic layer impedances η . Each matrix element of (4.2.5) models the (u-1)-th layer crossing through the phase shift

$$\delta_{u-1} = k_{(u-1)z} (z_{u-1} - z_u) = k_{(u-1)z} d_{u-1}$$
(4.2.10)

Where $k_{(u-1)z}$ and d_{u-1} are the layer wavenumber along z-axes and layer thickness respectively.

Following the above formalism, the overall multilayer reflection and transmission can be calculated through the simple matrix product:

$$\overline{V_{0,n}} = \overline{V_{0,1}} \cdot \overline{V_{1,2}} \cdots \overline{V_{n-1,n}}$$
(4.2.11)

Each matrix represents a material interface. In particular $\overline{V_{0,1}}$ is referred to last interface while $V_{n-1,n}$ is referred to the initial free-space and layer material interface met by the propagating electromagnetic wave.

Referring to (4.2.1), it is worth noticing that the number of material strata is exactly (n+1) - i.e., the number of interfaces plus one required to take into account the interface between last layer of the multilayer and the surrounding theoretically infinite medium (free space or PEC).

Now let us to consider the interface separating the last two regions n and n-1, in case of right-hand unbounded medium (often called as the multilayer coating) where the last-th layer is air we get for the last interface:

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$$\begin{bmatrix} E_n^+ e^{-jk_t z_n} \\ E_n^- e^{+jk_{t1} z_n} \end{bmatrix} = \frac{1}{2} \begin{pmatrix} 1 + \frac{\eta_n}{\eta_{n-1}} \end{pmatrix} \cdot \begin{bmatrix} 1 & R_{n,n-1} \\ R_{n,n-1} & 1 \end{bmatrix} \cdot \begin{bmatrix} E_{n-1}^+ e^{-jk_{n-1} z_{n-1}} \\ E_{n-1}^- e^{+jk_{n-1} z_{n-1}} \end{bmatrix}$$
(4.2.12)

Where:

since in our scenario n = 1 and n - 1 = 0 we have:

$$\overline{\overline{V_{1,0}}} = T_0^{-1} \begin{bmatrix} 1 & R_1 \\ R_1 & 1 \end{bmatrix}$$

Which gains symmetry and anti-symmetry properties, whereas in the case of a perfect electrical conductor (PEC) backed absorber, we find the unitary matrix:

$$\overline{\overline{V_{1,0}}} = \begin{bmatrix} 1 & 1\\ 1 & 1 \end{bmatrix}$$
(4.2.14)

Such a simplified forms is not retrievable from (4.2.7) directly, hence the application of boundary conditions is further required in deriving it. Once calculated the general matrix of (4.2.11) one can relate the fields impinging from unbounded left-hand medium to the field outgoing from the last interface. In case of unbounded right-hand medium, we obtain

$$\begin{pmatrix} E_n^+ \\ 0 \end{pmatrix} = \overline{V_{n,0}} \cdot \begin{pmatrix} E_0^+ \\ E_0^- \end{pmatrix} \quad \text{i.e.,} \quad \begin{pmatrix} E_n^+ \\ 0 \end{pmatrix} = \begin{bmatrix} V_{n,0}^{1,1} & V_{n,0}^{1,2} \\ V_{n,0}^{2,1} & V_{n,0}^{2,2} \end{bmatrix} \cdot \begin{pmatrix} E_0^+ \\ E_0^- \end{pmatrix}$$
(4.2.15)

Whereas in case of PEC medium, Eq. (4.2.15) turns into

$$\begin{pmatrix} 0 \\ 0 \end{pmatrix} = \begin{bmatrix} V_{n,0}^{1,1} & V_{n,0}^{1,2} \\ V_{n,0}^{2,1} & V_{n,0}^{2,2} \end{bmatrix} \cdot \begin{pmatrix} E_0^+ \\ E_0^- \end{pmatrix}$$
(4.2.16)

Drawing on representation of (4.2.22) or (4.2.23) it's straightforward to find a formal expression of reflection coefficient Γ at the first interface and of transmission coefficient *T*. They are defined as

$$\Gamma = \frac{E_0^-}{E_0^+} = -\frac{V_{n,0}^{2,1}}{V_{n,0}^{2,2}}$$
(4.2.17)

$$T = \sqrt{\frac{\eta_0}{\eta_n}} \frac{E_n^+}{E_0^-} = \sqrt{\frac{\eta_0}{\eta_n}} \left(V_{n,0}^{1,1} - V_{n,0}^{1,2} \frac{V_{n,0}^{2,1}}{V_{n,0}^{2,2}} \right)$$
(4.2.18)

As will be discuss later on the chapter, the employed algorithm can operate in different optimization-oriented modalities. The one toward the minimization of material thickness needs for the possibility of removing layers from the maximum allowed set. This means that, in bringing optimization, a layer could not be necessary anymore - i.e. no longer physically present - even though related interface matrixes are still required for product completion of (4.2.90). This is easy to figure out in automatic computation contexts: in other words, when an arbitrary layer is removed the *u*-th thickness $du = z_{u-1}-z_u=0$ tends to zero and Eq.(4.2.7) turns into the identity matrix:

$$\overline{\overline{V}_{(u-1),u}} = \frac{1}{\frac{2\eta_u}{\eta_u + \eta_{u-1}}} \begin{bmatrix} e^{-jk_{(u-1)z}(z_{u-1}-z_u)} & R_{(u-1),u}e^{-jk_{(u-1)z}(z_{u-1}-z_u)} \\ R_{(u-1),u}e^{+jk_{(u-1)z}(z_{u-1}-z_u)} & e^{+jk_{(u-1)z}(z_{u-1}-z_u)} \end{bmatrix} = (4.2.19)$$

$$= 1 \cdot \begin{bmatrix} e^{-jk_{(u-1)z}(0)} & R_{(u-1),u}e^{-jk_{(u-1)z}(0)} \\ R_{(u-1),u}e^{+jk_{(u-1)z}(0)} & e^{+jk_{(u-1)z}(0)} \end{bmatrix} = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$$

In such case we take $\eta_{u-1} = \eta_u$ and $n_{u-1} = n_u$ as a consequence and hence does not affect the crossing field. So, provided this rule is properly applied, matrix of Eq.(4.2.15) Eq.(4.2.15) are the only required for the implementation. One further critical occurrence to be taken into account is that of the last layer removal. If this happens, the last matrix form of (4.2.15) must shift backward to the previous interface of Eq.(4.2.11) and $\overline{V_{n,n-1}} = \overline{I_2}$; this procedure must be iterated when multiple layers close to the last interface are removed. Such type of check can be executed from the right to the left or vice versa as a function of the initial layer thickness checked at the start of the procedure. Oblique incidence can be easily accounted for upon insertion of TE and TM impedance form in Eq.(4.2.7).

5. Search algorithm adopted to design multilayer absorber

The most popular evolutionary algorithm is Genetic Algorithm (GA). GA attempts to simulate the phenomenon of natural evolution. In natural evolution, each species searches for beneficial adaptations in an ever-changing environment.

As species evolve, the new attributes are encoded in the chromosomes of individual members. This information does change by random mutation, but the real driving force behind the evolutionary development is the combination and exchange of chromosomal material during breeding [Mitsuo Gen, Runwei Cheng, 1999]. In this book an optimization algorithm called winning particle optimization (WPO) is proposed [D.Micheli et, al, 2010].

5.1 Winning particle optimization algorithm

Winning particle optimization (WPO), is a very simple algorithm, where at each time epoch of evolution, particle which best fit the objective function (OF), is deputed to pilot the trajectory of the remaining nonintelligent particles within the multidimensional space of solutions. In WPO, particles trajectories are simply defined by jumping of particles. Jumping is defined as coordinates sum or difference with respect to the current best fitting particle. The best particle represents the best position which defines the remaining particles search space and as a consequence, differently from the other particles, the best fitting particle is not subject to any displacement action within the iteration cycle. It must remain in a fixed position while the other particles jump around it, searching for a new potential best position in the space of solutions. At each WPO iteration, a new portion of the search space is explored and the same or most probably a new potential better fitting location for each particle is always found. In Fig. 5.1.1, WPO flow chart related to (5.1.1) is shown. At the beginning of the algorithm, particles are randomly distributed within the *n*-dimensional search space. After that at the first step of the WPO algorithm, evaluation of objective function (OF) for all the particles are computed. In the next step, particles are compared to each other using value of their objective function and the best fitting particle is marked with its proper index position. Each particle position is completely defined by its coordinates and their number represents the dimensionality of the space where particles jump in search of the optimal final solution. Trajectory of each particle, except that of the best fitting particle, is defined in the following way: if m-th-coordinate position of a certain particle P^k is lesser then the corresponding m-thcoordinate position of the current best particle PB4, then the new m-th-coordinate position will result from the sum of particle and best particle m-th-coordinates; while if m-th-coordinate position of a certain particle Pk is greater then the corresponding m-th-coordinate position of the current best particle PB_{q} , then the new m-th-coordinate position will result from the difference of best particle and particle m-th-coordinates;. Calling q the index of the best particle found at each iteration cycle, the condition which needs to be satisfied is $q \neq k$. Two different evolutions expressed by the Eq.(5.1.1) and (5.1.2), are possible, they define particles positions at i+1-th-iteration as a function of particles position at previous *i*-th-iteration. In the rest of work, method related to Eq.(5.1.2) has been applied.

$$P_m^k(i+1) = PB_m^q(i) + g \cdot \delta_m \cdot R_m \cdot P_m^k(i).$$
(5.1.1)

$$P_m^{\kappa}(i+1) = \delta \cdot R_m \cdot P_m^{\kappa}(i) + g \cdot PB_m^{q}(i)$$
(5.1.2)

where

 $g = +1 \text{ if } P_m^k(i) < PB_m^k(i)$ $g = -1 \text{ if } P_m^k(i) > PB_m^k(i)$ k = 1 to Particle Number $q = 1 \text{ to Particle Number and } k \neq q$ m = 1 to n n = Space Dimensions $R_m = \text{random number in the interval } [0 - 1]$ $\delta = \text{Convergenc eParameter}$

R is a random number in the closed range 0-1, which in random way adjust the amount of jumps for each single coordinate particle dimension. Such randomization helps the search phase of optimal solution. Convergence parameter δ is defined later; it helps the final convergence of the WPO algorithm. Even thought mutation operation has not been applied on the subsequent reported optimization it has to be noticed that mutation has been included in WPO algorithm. At the end of the WPO diagram, a boundary conditions check

for the new particles coordinates set is required in order to avoid to overcome the admitted constraints. The entire loop cycle can be iterated several times in order to get the required OF minimization.

When out of boundary conditions are verified for the *m*-th-particles coordinates, then, it could happen that some particles are forced to go toward the limit of search space.

During the evolution boundary conditions checking procedure is done and variables are set to *max* or *min* value of admitted range if the current value are respectively above or lower these limits. The WPO idea based on a quasi-random particles jumps system, assuring an effective method for solutions space exploration. In order to ease the WPO convergence, a mechanism which provide a progressive reduction of the maximum amplitude of jumps has been introduced and is identified by the triplet $\delta_r P_r \sigma$ parameters.

Calling *IN* the number of WPO iterations and supposing *i* the current *i*-th iteration, then the value of δ is given by the following equation:

$$\delta = \sigma \left(1 - \frac{i}{IN + 1} \right)^P. \tag{5.1.3}$$

In (5.1.3), the meaning of σ , *P* parameters stays in fast or slow convergence of the WPO algorithm. In particular the higher the σ , the greater the initial jumps amplitude and the greater the distances where particles start to explore the search space. As far as *P* is concerned the higher its value, the faster the convergence to a suboptimal solution i.e., local minimum or maximum. The higher the current iteration number, the lower the δ parameter value. Parameter δ is by the position of the current particle, as in (5.1.1) and (5.1.2). Example related to (5.1.1) is::

$$P_m^k = BP_m^q + R_m \cdot P_m^k \cdot \delta \quad P_m^k = BP_m^q - R_m \cdot P_m^k \cdot \delta .$$

In Fig. 5.1.2, sequence of pictures shows the convergence of WPO algorithm for some canonical test functions [Franciszek Seredynski1, Albert Y. Zomaya, and Pascal Bouvry]: Sphere, Rastrigin, Griewank, Rosembrok, Akley, is shown. Parameter, is decreased with the iterations IN using $P = \sigma = 1$. Two different scenarios are compared, the first referring to Iteration Number (IN) = 500, Dimensions of Space Solution (DIM)=20, Number of exploring agents (Num Agents)=20; while the second referring to Iteration Number(IN)=500, Dimensions of Space Solution (DIM)=60, Number of exploring agents (Num Agents)=100.

In order to evaluate the robustness of WPO algorithm, for each test function, the algorithm as been tested repetitively for twenty times.

In Table. 5.1.1. and 5.1..2, the mean and standard deviation values are shown for two different scenario, the first referring to Iteration Number (IN)=500, Dimensions of Space Solution (DIM)=20, Number of exploring agents (Num Agents)=20; while the second referring to Iteration Number (IN)=500, Dimensions of Space Solution (DIM)=60, Number of exploring agents (Num Agents)=100.

It can be noticed that convergence difficulties increases for Rastrigin and Rosembrok test functions when the dimension of solution space changes from 20 to 60.



Fig. 5.1.1. WPO flow chart



Fig. 5.2.2. a),b),c),d),e) Typical Objective Function minimization with: IN=500, DIM=20, AGENT=20 and f),g),h),i),l) Typical Objective Function minimization with: IN=500, DIM=60, AGENT=100.

TEST Function	Theoretical Convergence value	WPO Mean Values Dim=20 NAgent=20	WPO Standard Deviation Dim=20 NAgent=20	WPO Mean Value Dim=60 NAgent=100	WPO Standard Deviation Dim=60 NAgent=100
Sphere	0	0	0	0	0
Rastrigin	0	0	0	0	0
Griewank	0	0	0	0	0
Rosenbrok	0	56.1	0.7	56.1	0.7
Akley	0	0	0	0	0

Table 5.1.1. WPO Test: IterNumber=500, DIM=20 and 60, NumAgent=20 and 100, RunRipetition=20.

5.2 Absorber multilayer structure optimized by winning particle optimization

In Fig. 5.2.1, a design of an absorber in the 5-18 GHz band is shown. In particular the optimization has been conducted by the WPO algorithm, taking onto account for both: microwave loss factor maximization expressed in (4.2.1) and multilayer thickness minimization [D.Micheli et, al,. 2010]. In Fig. 5.2.1. a,b) reflection coefficient TE,TM remain below -10 dB for incidence angles in the range 0°-40° in the most part of the bandwidth (5.38-18 GHz).

In Fig. 5.2.1 b), it can be observed that for incidence angle of 20°, 30°, 40°, 60°, TM reflection coefficient is lower than that at 0° incidence angle. Such angles are the Brewster angles for a lossy material more often referred to Zenneck angles [Sophocles J.Orfanidis, 2009].

In Fig.5.2.1 c,d), transmission Coefficient TE, TM remain below -15 dB within all the bandwidth and linearly decrease with the frequency as expected.

In Fig.5.2.1. e) minimization of objective function is shown, it can be observed that after the 550 *i*-th iteration the convergence of WPO algorithm doesn't evolve towards lower values and as a consequence toward better solutions. In Fig. 5.2.1 f), the absorber multilayer structure is schematically shown. It can be observed two type of absorber mixed together the first where the intrinsic layer impedances decrease from the top to the bottom of absorber and the second where an high layer impedance (resin) is put between lower impedance layers (MWCNTs), recalling in mind resonant absorbers behaviour.

6. Experimental validation of mathematical model for microwave absorbers design

In order to experimentally validate the mathematical model and the design method described in previous sections, we realized and tested several multilayer square tiles, one made of graphite and the others made of MWCNTs. Tiles structure, their dimensions and reflection loss results (dB), are shown in Fig. 6.1.

In order to test the reflection loss of tiles we built an in-house NRL arch measurement, also called bi-static reflection method [Umari, M. H. et al.]. In this configuration, two antennas are used for transmitting and receiving signals respectively, and the microwave reflectivity at different incident angles can be measured. The NRL Arch is the industry standard for testing the reflectivity of materials. Originally designed at the Naval Research Laboratory



Fig. 5.2.1. a,b) Reflection coefficient (dB) TE, TM of absorber, c,d) Transmission coefficient (dB) TE, TM of absorber, e) WPO minimization of objective function which takes into account for both: loss factor and thickness, f) scheme of absorbing multilayer structure made of carbon composite material.



Fig. 6.1. a) Graphite based tile of 10.9 mm thickness; b) MWCNTs based tile of 6.97 mm thickness; b) MWCNTs based tile of 6 mm thickness.

(NRL), the NRL Arch allows for quick, repeatable and non-destructive testing of microwave absorbent materials over a wide frequency range. Reflectivity is defined as the reduction in reflected power caused by the introduction of an absorbent material. This reduction in power is compared to a '*perfect*' reflection which is approximated very well by the reflection of a flat metallic plate. Antennas can be located anywhere on the arch to allow measurements of performance at off normal angles of incidence. Vector network analyzer is
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used for measurements to provide both the stimulus and the measurement. Calibration is performed by measuring the resultant power reflecting off the metal plate over a broad frequency range. This is established as the 'perfect' reflection or 0 dB level (i.e. the reference level). The material under test is then placed on the plate and the reflected signal measured in dB. Time domain gating may be used to eliminate antenna cross talk and reduce the error introduced by room reflections. Using this configuration, the properties of materials at different directions can be characterized. It should be noted that in bi-static reflection measurements, the reflection is dependent on the polarization of the incident wave. Incident waves with parallel and perpendicular polarization usually result in different reflection coefficients. In Fig. 6.2, bistatic measurement system and the tiles in composite material are shown. In this configuration, bistatic measurement system has been based on Agilent software 8571E (material measurement), and Agilent PNA-L vector analyzer. Antennas were bought at Q-par Angus Ltd and are in the range 8-12 GHz. After calibration, measurement of a known sample consisting in ECCOSORB AN73 absorber, [www.eccosorb.com], has been performed in order to be aware about errors in the NRL measurement setup. Confidence of measurements was within 2 dB of interval with respect to reflection properties declared in ECCOSORB data sheet. At the end measurements of the manufactured samples have been performed for TE and TM mode. In Fig. 6.2, comparison between measured and simulated RAM structures is shown. It can be noticed that simulated curve shows similar behaviour with respect to measured one. Discrepancies in reflection loss data are around 2 dB, which is an acceptable accuracy in such kind of measurements.



Fig. 6.2. a) bistatic measurement system sheme, b) bistatic measurement system located at (www.saslab.eu).

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Magnetic Nanocomposite Devices for Cancer Thermochemotherapy

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1. Introduction

The combination of nanotechnology and medicine has yielded a very promising offspring that is bound to bring remarkable advance in fighting cancers. In particular, nanocomposite materials based novel nanodevices with bi- or multi- clinical functions appeal more and more attention as such nanodevices could realize comprehensive treatment for cancers. Because it can provide an effective multimodality approach for fighting cancers, cancer comprehensive treatment has been fully acknowledged. Among the broad spectrum of nanoc-biomaterials under investigation for cancer comprehensive treatment, magnetic nanocomposite (MNC) materials have gained significant attention due to their unique features which not present in other materials. For instance, gene transfection, magnetic resonance imaging (MRI), drug delivery, and magnetic mediated hyperthermia can be effectively enhanced or realized by the use of magnetic nanoparticles (MNPs) (Shinkai 2004; Ito 2005). Therefore, MNPs are currently believed with the potential to revolutionize the current clinical diagnostic and therapeutic techniques.

In therapeutic oncology, nanothermotherapy is one of the effective approach based on MNPs, which can be achieved by applying nanoscaled metallic particles that convert electromagnetic energy into heat, for instance, magnetic fluid hyperthermia (MFH) mediated by superparamagnetic iron oxide nanoparticles (SPIONs) (Gazeau 2008). Upon exposure under alternative magnetic field (AMF), SPIONs can generate heat through oscillation of their magnetic moment (Figure 1).Currently, clinical trials at phase II are now under investigations for MFH on patients in Germany and Japan and demonstrate very inspiring for cancer therapy (Ito 2008). Except for nanothermotherapy, another possible and most promising application of MNPs is in drug delivery as carriers for chemotherapeutic agents for sustained or controlled delivery for cancer treatment. Compared with the organic materials including polymeric nanoparticles, liposomes and micelles under investigation as drug delivery nanovectors, the main advantages of MNPs as drug carriers summarized by

Manuel Arruebo can be: (i) visualized (SPIONs for MRI); (ii) guided by means of permanent magnetic field; and (iii) heated in a magnetic field to trigger drug release and/or combined with hyperthermia (Arruebo 2007). These advantages can help to yield an improved treatment efficacy and reduction of unwanted side effects. Moreover, it should be particular to point that the later capacity of MNPs is of special significance as the hallmarks of hyperthermia and its pleotropic effects are in favour of its combined use with chemotherapy (Issels, 2008). Therefore, hyperthermia and chemotherapy can be integrated into unique formulations or devices through smart engineered MNC materials, which enabling simultaneously thermochemotherapy and thermochemotherapy, we will review the design and fabrication strategies for the development of MNC devices for thermochemotherapy.



Fig. 1. Scheme of magnetic nanothermotherapy mediated by SPIONs

2. Magnetic nanothermotherapy

"Quae medicamenta non sanat; ferrum sanat. Quae ferrum non sanat; ignis sanat. Huae vero ignis non sanat; insanabilia reportari oportet" (Those diseases which medicines do not cure, the knife cures; those which the knife cannot cure, fire cures; and those which fire cannot cure, are to be reckoned wholly incurable).

- Hippocrates of Kos (ca. 460 BC - ca. 370 BC), Western father of medicine

From aphorism by Hippocrates, he believed that diseases could be cured by raising the patient's body temperature. Although the biological effectiveness of heat in treating cancer has been fully recognized for decades, and many of its molecular mechanisms are elucidated, however, in oncology clinical hyperthermia is currently regarded as the forth method of therapy after surgery, chemotherapy and radiotherapy (Hilderbrandt 2002). Technical challenges associated with the currently available hyperthermia modalities can explain the seemingly inconsistency, which may include: (i) the difficulty of the uniform heating only within the tumor region until the required temperature is reached while without damaging the normal tissues nearby, and (ii) the inability to create hyperthermia uniformly throughout the tumor volume (Saniei 2009). While the former may bring some unwanted side effect of the treatment or unnecessary harm to the patient, the later would leave defective cells unharmed, thus resulting in relapse of the tumor. Therefore, the development of novel hyperthermia technique capable of specifically targeting tumor tissue and cells is highly desired.

Application of nanotechnology has become central focus on cancer treatment and it also offers new opportunities and innovative solutions to hyperthermia. The marriage of nanotechnology and hyperthermia has yielded nanothermotherapy that is set to bring momentous advance in the fight against cancers. As mentioned above, this can be achieved by the design of nanometric heating-generating 'foci' which can be activated remotely by an external AMF (Gazeau 2008). As a completely new approach for targeted cancer treatment, nanothermotherapy couples the energy magnetically (through Brownian relaxation or Neel relaxation) to nanoparticles only within cancer tissue. In this way, nanothermotherapy aims at treating cancer from the cellular or intracellular level, as it is intended the design of nanostructured devices capable of penetrating selectively into cancer cells in order to generate lethal heating from the cell inside. This process can lead to direct killing of the local quickly, specifically and homogeneously, tumor tissue in the meanwhile, nanothermotherapy can also effectively activate the immune system to attack distant tumor site, a phenomenon known as abscopal effect in cancer treatment.

The external AMF applied in the treatment belongs to low or middle frequency electromagnetic (EM) field. Currently, EM radiation has been considered as a fundamental tool in cancer therapy, especially for diagnosis such as MRI and positron emission tomography (PET) as it is well accepted that EM fields are not especially contraindicated for humans (Goya 2008). The therapeutic potential of EM can be further explored in the magnetic nanothermotherapy and the magnetic field applicators at frequencies and field values are with full compliance to the safety regulations demanded in clinical applications. Safety demand is also the prerequisite criterion for MNPs therefore there is a multitude of known MNPs strongly restricted by the demand of non-toxicity and biocompatibility for the consideration of clinical applications. Normally investigations are focused on magnetic iron oxides Fe₃O₄(magnetite) and γ -Fe₂O₃(maghemite) which have been proved to be well tolerated by the humans.

Currently, the worldwide first magnetic nanothermotherapy against brain tumors, termed as Nano-Cancer® therapy is now under investigation in a phase-II study. Preliminary results show evidence of a local effectiveness and with only minor to moderate side effects. Besides the clinical trial, *In vitro* and animal experiments regarding MFH are widely carried out worldwide. Table 1 summarizes the major events associated with the development of magnetic nanothermotherapy.

3. Thermochemotherapy: thermal enhancement of drug cytotoxicity

In clinical, hyperthermia is usually applied as an adjunct treatment to an already established treatment modality such as chemotherapy, as hyperthermia can effectively enhance the cytotoxicity of various antineoplastic agents (thermal chemosensitization). In several clinical phase-III trials, an improvement of both local control and survival rates have been demonstrated by adding local/regional hyperthermia to chemotherapy in patients with locally advanced or recurrent superficial ad pelvic tumors. Additional application of selected chemotherapeutic drugs has been shown to enhance the inhibition of clonogenic cell growth at elevated temperatures both *in vitro* and in animal experiments. Thermal enhancement of drug cytotoxicity is accompanied by cellular death and necrosis without increasing its oncogenic potential. It also has been recognized that mechanisms for the thermal enhancement include increased rate constants of alkylation, increased drug uptake and inhibition of repair of drug-induced lethal or sub-lethal damage, etc. Generally,

Time	Milestone Events			
1957	The concept of MMH was initially described by Gilchrist et al (Gilchrist 1957)			
1959	MMH with magnetic particles was carried out on rabbits in which inguinal lymph modes were successfully targeted with heat (Medal 1959)			
1979	The concept of intracellular hyperthermia was first proposed by Gondon et al (Gondon 1979)			
1993	Jordan A et al published the first fundamental work describing the real potential of magnetic fluids for hyperthermia (Jordan 1993)			
2003~2005	MagForce Nanotechnology AG carried out the phase I clinical trials of MFH in Germany (Hauff-Maier 2007; Johannsen 2007; Wust 2006)			
2005	MagForce Nanotechnology AG initiated the Phase II clinical trials of MFH in Germany			
2008	The concept of Nanothermotherapy was first proposed (Gazeau 2008)			
2009	¹⁹ The first report of post-mortem neuropathological findings of GBM patients undergone MFH was reported (Landeghem 2009)			
2009	Ethical discussion on MFH for brain cancer was published (Muller 2009)			

Table 1. Major events associated with the development of MMH.

supported by a wealth of biomedical and molecular biological data, the results of clinical trials strengthen the current evidence that hyperthermia combined with chemotherapy is an effective and practical modality which should be integrated in the present cancer treatment armamentarium (Issels 2008).

4. Design, fabrication and evaluation of magnetic nanocomposite devices for thermochemotherapy

In recognition that MNPs can be acted simultaneously as mediators for magnetic nanothermotherapy as well as drug carriers, it is thus highly feasible to design and fabricate drug incorporated MNC devices for multimodal cancer treatment of thermochemotherapy, to realize the possible thermal enhancement to drug cytotoxicity. As MNPs comprise the 'scaffold ' of the nanocomposite devices, we will first address the protocols for the synthesis and surface modification of MNPs, and then design and fabrication strategies of the MNC devices will be described.

4.1 Synthesis and surface modification of MNPs

As mentioned above, iron oxide is the material under close investigation for medical application due to its superior biocompatibility with respect to other magnetic materials. Apart from biocompatibility, high magnetization, small size (less than 100nm), and narrow particle size distribution are also key factors for MNPs to be applied in nanothermatherapy. For this purpose, dozens of protocols for SPION synthesis have been developed in recent years, including co-precipitation, organic phase synthesis, solvothermal synthesis, etc. The simplest, cheapest and most environmentally-friendly procedure by far is based on the co-precipitation method, which involves the simultaneous precipitation of Fe²⁺ and Fe³⁺ in basic aqueous media.

Since the as-synthesized SPIONs in the colloidal form (known as ferrofluid or MF) have a large surface area to volume ratio, they are easily to undergo aggregation to form large

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Fig. 2. TEM images of the Fe_3O_4 nanoparticles. a: surface modified with oleate sodium; b: un-modified nanoparticles

clusters. Therefore, surface coating or modification is required to improve the properties of the MF, such as stability and dispersity. Figure 2(a) illustrates the high-resolution transmission electron micrographs (TEM) of Fe_3O_4 nanoparticles. Due to the large specific surface area, high surface enery, and magnetization of the MNPs, the un-modified nanoparticles were severely aggregated (Figure 2(b)). However, after surface modification by sodium oleate, the nanoparticles are almost mono-dispersed with seldom aggregation. Stability of the MF can also be significantly enhanced and the MNPs are able to suspend in aqueous environment stably for months after surface modification. Besides, inductive heating capacity of MNPs, a vital issue related with nanothermotherapy can be greatly promoted by proper modification. Except for physical and chemical properties of the MNPs, endocytosis or cell uptake of the MNPs can be optimized and it has been reported that the aminosilan coated MNPs would be taken up by prostate carcinoma cells but not by normal prostate cells. All the findings strongly suggest surface modification plays critical roles in the properties of MNPs and therefore to this end, great attentions have been paid on choosing appropriate coating materials for functional modifications of SPIONs and detailed information can be referred to the careful reviews (Mornet 2004; Gupta 2005; MCCarthy 2008; Sun 2008).

4.2 Magnetic nano-drug by surface modification chemistry for cancer thermochemotherapy

In relation to the multi-therapy modality of thermochemotherapy, the intention for the design of nanocomposite devices is to use MNPs as one single tool for the combination of hyperthermia and chemotherapy to reach an enhanced therapeutic effect. So far there have been developed series protocols on how to engineer the two moieties within a single nanoplatform. Magnetic nano-drug by surface modification chemistry represents a kind of formulation to conjugate or attach drug molecules to the surface of MNPs. A number of physical or chemical approaches have been developed for the conjugation or attachment of functional molecules with MNPs surface which can be categorized into covalent linkage and physical interactions.

Physical interactions mainly include electrostatic, hydrophilic/hydrophobic and affinity interactions. For some charged drug molecules, electrostatic interactions have particularly useful in the assembly of magnetic nano-drugs, for instance, cisplatin-functionalized MNPs. Cisplatin belongs to platinum-based chemotherapy drug used to treat various types of cancers. It can form irreversible crosslink with bases in the DNA and ultimately triggers

apoptosis. It has been approved by US FDA for the treatment of a variety of malignancies including testicular, ovarian, bladder, small cell lung, as well as head and neck cancers. To fabricate cisplatin magnetic nano-drug, the SPIONs cores were coated by a soluble starch derivatives so that particles were negative charged with zeta potential of -41my, allowing electrostatic binding of positively charged aquated cisplatin molecules (molecular structure shown in Figure 3). The binding process is rapid with high efficiencies. It was reported the prepared cisplatin magnetic nano-drug demonstrated ideal inductive heating property under AMF. A temperature increase of 47.3K was observed under AMF within 3 minutes, which is adequate for hyperthermia treatment (Kettering 2009). Besides, heating can also promote a rapid release of cisplatin from the MNPs. Babincova ever reported that under the influence of magnetic heating, almost all the drug could be released after 20min, in contrast to the spontaneous release of cisplatin that was only 20% after this time (Babincova 2008). This cisplatin release will be favorable for successful chemotherapeutic activity and should increase the therapeutic effect of magnetic heating treatment in medicinal application. In vitro cytotoxicity of the combined treatment by the cisplatin magnetic nano-drug has been carried out on the treatment of BP6 rat sarcoma cells and the results showed that the combination therapy is strongly synergistic.



Fig. 3. Molecular structure of Cisplatin (left) and aquated cisplatin (right)

Compared with physical interactions, a much broader spectrum of approaches have been developed based on the covalent linkage or chemical coupling strategy. In a most recent review paper, Veiseh et al summarized that covalent linkage mainly comprises three approaches: direct nanoparticle conjugation, click chemistry and covalent linker chemistry (Veiseh 2010). Unique advantages and drawbacks of each of the three approaches were addressed in detail. Here, we report the fabrication and characterization of epirubicin-immobilized magnetic nano-drug that may potentially be applied for thermochemotherapy. Epirubicin (molecular structure shown in Figure 4) is an anthracycline drug used for chemotherapy which acts by intercalating DNA strands. Intercalation results in complex

chemotherapy, which acts by intercalating DNA strands. Intercalation results in complex formation which inhibits DNA and RNA synthesis. It also triggers DNA cleavage by topoisomerase II, resulting in mechanisms that lead to cell death. In order to immobilize the epirubicin molecules onto the surface of MNPs, conjugation strategy by linker chemistry was adopted. Briefly, polyarylic acid (PAA) was applied as the coating material to introduce carboxyl groups onto the SPIONs surface. The amino group of epirubicin can be conjugated with SPIONs via amide bond by applying the carbodiimides (EDC) and Nhydroxysuccinimide (NHS or sulfo-NHS) as the chemical linkers. The immobilization scheme of the conjugation was illustrated in Figure5.

Figure 6 demonstrates the shape, size and degree of uniformity of the PAA modified and epirubicin immobolized SPIONs. Both SPIONs are spherical in shape, mono-dispersed with diameter around 10nm. There is no significant change in size after epirubicin conjugation. X-ray powder diffraction patterns of epirubicin conjugated SPIONs was shown in Figure 7. From the pattern of the sample, it was found that there were a series of characteristic peaks at 2.968(220), 2.535(311), 2.103(400), 1.719(422), 1.614(511) and 1.478(440), demonstrating the







Fig. 5. Immobilization scheme of the conjugation of epirubicin and SPIONs by applying EDC/Sulfo-NHS as chemical linkers



Fig. 6. Morphology of MNPs by TEM (left: PAA-MNPs; right: EPB-PAA-MNPs)

patterns were well indexed to the inverse cubic spinel phase of Fe₃O₄. This suggested that conjugation of epirubicin to the SPIONs has no effect on the crystalline structure of the SPIONs cores. The VSM measurement of magnetization of the epirubicin-MNPs at 300K is also shown in Figure 7. It can be seen from this figure that the MNPs show supermagnetic characteristics with zero hysteresis cycle. No coercive field and remnant magnetization can be observed. However, the magnetization was remarkably decreased by the conjugation of epirubicin onto the SPIONs.





The heating profiles of the epirubicin-MNPs suspensions with different MNPs concentrations under AMF of 300kHz were shown in Figure 8. As can be seen in Figure 8, higher particle concentration results in a greater increase in the temperature. The desired temperature can be achieved by appropriate adjusting the MNPs concentration.

Effect of heating on the epirubicin release was shown in Figure 9, which clearly demonstrated that under the influence of magnetic heating, almost all the drug can be released after 48 hour, in contrast to the spontaneous release of epirubicin that was only 50% after this time period. In vitro evaluation of the thermochemotherapy mediated by epirubicin-MNPs was carried out by the treatment of human gastric cancer SGC-7901.The viability data of SGC-7901 cells subjected to mono- treatment by epirubicinl and nanothermotherapy, as well as bi-modal treatment by thermochemotherapy are summarized in Figure 10. Assessment of viable SGC-7901 cells after various treatments showed mono-treatment treatment by hyperthermia or epirubicin released from magnetic nano-carrier could cause retarded proliferation on the cells. When the bi-modal treatment was applied on the cells, an even significantly greater decrease can be noticed on the cell viability (p<0.05), indicating an intensity effect of nanothermotherapy on epirubicin treatment. Although in vivo investigation should be carried out for the validation of the formulation, the findings we report here strongly support that drug conjugated MNC fabricated by covalent linkage is feasible for a combined thermochemotherapy in the cancer treatment.



Fig. 8. Heating profiles of the epirubic in-MNPs suspensions with different MNPs concentrations under AMF of $300 \rm kHz$



Fig. 9. Effect of heating on the epirubicin release from the EPB-MNPs



Fig. 10. Comparison of different treatment modality on the SGC-7901 cell viability

4.3 Solar-planet structured magnetic nanocomposite devices for cancer thermochemotherapy

Although surface modification chemistry provides a versatile tool for conjugating the drug molecules onto the MNPs surface, there is still some restrictions for this strategy. It was suggested by Veiseh et al that the choice of chemistry should be dictated by the chemical properties and functional groups found on the SPION coating and ligand to be linked (Veiseh 2010). For most of the drug molecules, there are no proper functional groups nor is it convenient to introduce such a functional group onto the MNPs surface for further conjugation. Besides, SPIONs applied in nanothermotherapy are normally hydrophilic, whilst there are numerous drugs are not soluble in water, therefore it is very challenging to find an appropriate medium to carry out the modification chemistry. We thus report here so-called solar-planet structured MNC devices for the combined thermochemotherapy. In the present study, docetaxel is used as a model small molecule anticancer drug, which is a poorly water-soluble, semi-synthetic taxane analog commonly used in the treatment of breast cancer, ovarian cancer, small and non-small cell lung cancer, prostate cancer. For the purpose of fabricating the solar-planet structured MNC devices, docetaxel loaded polymeric nanoparticles (DNPs) composed of carboxylic-terminated poly(D,L-lactic-co-glycolic acid) (PLGA) with Vitamin E TPGS as emulsifier for sustained drug release were prepared by a modified solvent extraction/evaporation technique. Intensive investigations have been carried out for the DNPs and the detailed fabrication protocols of DNPs could be found from the published work (Feng 2007). The size of the DNPs fabricated by solvent evaporation method is around 200nm. Furthermore, the MNPs modified with amino groups could be covalently attached to the surface of carboxylic terminated DNPs to form the socalled solar (DNPs)-planet (MNPs) structured MNC by EDC/NHS crosslinking protocol as illustrated in Figure 5.

TPGS-emulsified PLGA nanoparticles were found more advantageous than any other kind of PLGA nanoparticles in resulting much higher drug EE, cellular uptake, and *in vitro* cancer cell cvtotoxicity, and more desirable in vivo pharmacokinetics. The nanoparticles were found to be spherical with diameter of 200nm (Figure 11), which are close to the optimum size for cellular uptake in vitro. Before carrying out in vitro and in vivo investigations on the novel nanocomposite for thermochemotherapy, fluorescent observation was applied to confirm the formation of the solar-planet structured MNC. Firstly, docetaxel loaded PLGA NPs were labelled with coumarin-6 as the fluorescent marker. After the conjugation of the aminocoated MNPs and the fluorescent PLGA NPs, the product was collected by the permanent magnet and then underwent thorough washing for at least 3 times by DI water. The suspension was then subjected for fluorescent observation. It is clearly demonstrated from Figure 12 that there is much stronger fluorescent intensity compared with the control group, where there was no the linker molecules EDC/NHS during the conjugation. This observation strongly confirmed the formation of the so-called solar-planet structured MNC. Our in vitro analysis has demonstrated the thermal enhancement on docetaxel cytotoxicity can be achieved by the solar-planet structure MNC (data not shown). Further on, this novel nanocomposite device was applied in vivo to evaluate the effect of themochemotherapy on the tumor bearing nude mice. The temperature for hyperthermia was controlled around 46°C and the drug was administered at 10mg/kg dose. The time course of C6 tumor nodules growth subjected to different treatment was shown in Figure 13, which is obviously demonstrated that the tumor volume of the mice in the control group steadily increased with no evidence of regression. While both mono-treatment of thermotherapy and



Fig. 11. SEM images of docetaxel loaded polymeric nanoparticles



Fig. 12. Fluorescent observation of conjugation MNPs with DNPs by covalent linker chemistry with (left) and without (right) the application of EDC/NHS as chemical linkers.



Fig. 13. Tumor growth of C6 cells in non-treated control mice (n = 10), mice treated with nanothermotherapy (n = 10, T=46 $^{\circ}$ C), mice treated with docetaxel (dose=10mg/kg) and mice treated with themochemotherapy. Points, mean tumor volume (mm³); bars, SD.

chemotherapy can greatly inhibit the *in vivo* tumor growth, tumor volume in the group of bi-modal treatment mediated by the novel MNC was significantly reduced compared with chemotherapy (p<0.05) and control group (p<0.001). Our observation supports that solar-planet structured MNC is a novel and effective mediator for magnetic thermochemotherapy. The MNC can realize cancer comprehensive treatment thus has great potential in clinical application.

4.4 Drug loaded magnetic nanocomposite biodegradable implants for cancer thermochemotherapy

Either the magnetic nano-drug or the solar-planet nanocomposite discussed above is in the injectable formulation. The particles are dispersed in the aqueous continuous phase (most often PBS buffer) to form a stable nanocomposite colloid or suspension. For clinical application, the colloid or suspension can be administered by direct injection, arterial infusion or intravenous infusion. However, in some cases the injectable formulations may result in limited clinical effectiveness, for instance, post-surgical local cancer treatment for malignant gliomas. Malignant gliomas such as glioblastoma multiform (GBM) characterized by aggressive proliferation of undifferentiated cells, pervasive invasion into distant healthy brain tissue and a high penchant to recur is among the most recalcitrant tumors to be treated. Currently, surgical debulking of the accessible tumor from the patient's brain is the conventional clinical treatment for glioma. However, the amount of tumor removed is often limited by proximity to critical regions for brain function, thus resulting in risk of tumor regrowth from residual tumor. In clinical, cancer remission can be limited by conventional systemic post-surgical treatment and for this purpose, biodegradable controlled release polymeric implants could be surgically located at the site of tumor removal during the debulking surgery.

It is well acknowledge that the use of surgically implanted local release systems made of biodegradable polymers for drug delivery over extended periods of time has good potential in glioma treatment. Gliadel® (polifeprosan 20 with carmustine implant) has been approved by the US FDA for use in post-surgical local chemotherapy against recurrent malignant glioma. However, despite its potential, clinical trials with commercial Gliadel® wafer delivering carmustin vs. Placebo wafers have been shown to small improvements in median survivability of patients diagnosed with high-grade malignant gliomas from 11.6 to 13.9 months, and from 4.6 to 6.4 months for recurrent cases. In response, Ranganath et al have explored the controlled release of alternative chemotherapeutic agents (paclitaxel) and fadiosensitization (etanidazole) for treatment (Ranganath 2010). Since the advantages for comprehensive cancer treatment has been recognized, it is thus highly significant to develop composite polymeric surgical implant to achieve multimodality approach for fighting cancers. In principle, such kind of treatment can be realized by applying of the tailored magnetic nanoparticles (MNPs) composite polymeric film. Fe₃O₄ MNPs acting as the agent for MMH, and anti-cancer drug docetaxel as chemotherapeutic agent were incorporated within the biodegradable polymeric film (Zhao 2009).

Figure 14 gives the observations of the MNC film prepared by the solvent evaporation method. Poly (D, L) lactide-trimethylene carbonate (PLA-PTMC) copolymer was employed as the film matrix, as its inhibitive effect of adhesion formation after surgery has been confirmed. The film is flexible, smooth and homogeneous. Figure 2 also indicated a

morphology difference between the nanocomposite film surfaces of air-solvent interface and solvent-substrate interface. With the evaporation of the solvent and under the action of gravity, the MNPs would be precipitated out and deposited onto the substrate forming a rather rigid and homogeneous surface. On the other side, with a higher solubility with solvent, PLA-PTMC tends to concentrate at the air-solvent interface and formed an immiscible blending/mixture with MNPs clusters, which result in the roughness formation. It is worth mentioning that such a rough surface would be more significant for facilitating drug release from the polymeric matrix. The heating profiles of the nanocomposite polymeric films with different MNPs contents under AMF of 300kHz were shown in Figure 15. It is obvious to notice that the heating curve exhibits an asymptote, which signals the equilibrium of the heating process. The curves show the final temperatures upon equilibrium (Te) depend strongly on the MNPs contents, i.e. higher magnetic particles content within the film can ensure a higher Te. Another decisive factor for the heating process is the magnetic field intensity. As can be seen in Figure 15, higher field intensity



Fig. 14. SEM images of nanocomposite films (left: MNPs nanocomposite film(50% MNPs loading and 5% docetaxel loading) at solvent-substrate interface; right: same nanocomposite film at air-solvent interface)



Fig. 15. Inductive heating profiles of nanocomposite films under AMF at different field intensity (left: with 50% MNPs; right: with 25% MNPs)



Fig. 16. In vitro drug release profile of docetaxel (5% drug loading)

results in a greater increase in the temperature, which means more energy can be generated by the MNPs within the films. The desired temperature can be achieved by appropriate choosing the MNPs content or adjusting the field intensity. All of these can guarantee the temperature requirement for the hyperthermia for cancer treatment. The release profiles of docetaxel from the polymeric films in 14 days were investigated and the results are shown in Figure 16. In general, the release of docetaxel from the films was characterized by an initial rapid release phase followed by a slower release phase. Figure 16 also demonstrates 20min exposure of the film under AMF would greatly facilitate the docetaxel release from the film. This phenomenon may be attributed to the accelerated diffusion of docetaxel from the film to the PBS buffer upon heating generated from AMF exposure.

Both in vitro and in vivo studies have been carried out for the evaluation of the biocompatability, cytotoxicity and anti-cancer effectiveness of themochemotherapy mediated by the MNC film. Biocompatability of the prepared nanocomposite film has been fully confirmed by in vitro and in vivo investigations. Assessment of viable C6 cells after various treatments showed treatment by docetaxel released from film could cause retarded proliferation on the cells. When the bi-modal treatment by combination of MIH and chemotherapy was applied on the C6 cells, an even significantly greater decrease can be noticed on the cell viability (p<0.01, data not shown), indicating an intensity effect of MIH on docetaxel treatment. The in vivo study was performed tumor bearing nude mice. Xenografts of human glioma cell lines would be established by subcutaneous inoculation of U251 MG cells into the hind legs of BALB/c nude mice. For animals under placebo and experimental groups, a small incision by aseptic surgery was performed on the skin and tumor was reached after which 3/4 tumor volume would be carefully excised. The film discs would then be implanted well onto the residual tumor bed and subsequently the wound would be closed using subcutaneous suturing. Mice were then exposed under the AMF for 30mins treatment and the temperature of the tumor site was about 46°C. The body temperature was not affected and the mice did not have symptoms of dehydration and all survived the whole experiment of two weeks. Tumors in the thermochemotherapy group shrunk most significantly, as compared with those of the control groups and hyperthermia treatment only.



Fig. 17. The clinical photography of the tumor of mice under different treatment after 10 days (left: control; middle: hyperthermia (46°C) only and right: Thermochemotherapy by the nanocomposite film (46°C, docetaxel dose=10mg/kg).

5. Conclusion

In this chapter, various MNC devices for cancer thermochemotherapy are discussed and the detailed structures are summarized and illustrated in Figure 18. Except for the abovementioned MNC devices, drug encapsulated magnetic cationic liposome (MCL) and thermoresponsive core-shell MNPs are also under intensive investigation for the bi-modal therapy of combined hyperthermia with chemotherapy (Shinkai 2004; Purushotham 2010). The nanocomposite devices exhibit advantageous feature for a facilitated drug delivery from the nano-carriers and the magnetic mediated heating potential is adequate for hyperthermic treatments. We thus conclude that even though further detailed investigations are still necessary, tentative use in local tumor therapies aiming at a specific chemotherapeutic release in combination with magnetic heating is promising and feasible in the long term.



Fig. 18. Illustration of various MNC devices discussed in this chapter (a: Magnetic Nano-Drug by covalent linkage; b: Magnetic Nano-Drug by electrostatic interaction; c: solar-planet structured MNC; d: drug-loaded MNC film)

It is worth noting for the research and development on MNC devices for cancer thermochemotherapy discussed in this chapter, we only focus on the functions of MNPs as drug delivery carriers and mediators for MFH. Other features of MNPs, such as MRI contrast agent, gene transfection carriers as well as passive targeting driven by permanent magnet are not addressed here. Decisive understanding of the properties of MNPs will increase their potentials for medical applications, and the potentials of MNPs as unique platform for cancer diagnosis (MRI), nanothermotherapy, chemotherapy as well as gene therapy should be further explored to improve the medical techniques for cancer treatment.

6. References

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Electrokinetic Properties of Nanocomposite Fibres

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1. Introduction

Nanocomposite fibres are becoming of great importance since organic-inorganic nanoscale composites frequently exhibit unexpected hybrid properties synergistically derived from the two components.

The incorporation of one-, two- and three-dimensional nano particles, e.g. layered clays, nano-tubes, nano-fibres, metal containing nano-particles, carbon black, etc. is used to prepare nanocomposite fibres. However, the preparation of nanocomposite fibres offers several possibilities, i.e. creation of nanocomposite fibres by dispersing of nanoparticles into polymer solutions, the polymer melt blending of nanoparticles, in situ prepared nanoparticles within a fibre, the intercalative polymerization of the monomer, introduction of nanoparticles from dispersion into a porous polymer, preparation of nanocoatings by different techniques, e.g. sol-gel process, etc. With the respect to nanoparticles organization in / on fibres, respectively nanocoated fibres and fibres with nanoinclusions can be divided.

Nanocomposite fibres demonstrate improved applicable properties, e.g. mechanical, flammability, electromagnetic, electro-conductive, sorption properties, and/ or obtain additional functional properties, like antimicrobial, self-cleaning, shielding, UV protective properties, etc. Combining polymer fibre and nanopaticles of different structures and characteristics influences also fibre's surface properties, i.e. morphological properties and electrokinetic behaviour.

In order to analyse fibre's surface charge, the zeta potential is often determined through streaming potential measurements as a function of pH. These properties are generated by the electrochemical double layer (EDL), which exists at the phase boundary between a solid and a solution containing ionic moieties. By variation of the solution's pH value and electrolyte content it is possible to estimate the acidic / basic and polar / nonpolar character of the solid surface from zeta potential data.

Some examples of nanocomposite fibres (e.g. nanofilled PP fibres, SiO_2 – nanocoated different types of fibres) regarding their electrokinetic properties are presented in the contribution. In addition to, the influence of nanocomposite fibres preparation procedure conditions on their zeta potential values is demonstrated.

2. Nanocomposite fibres

Functional textiles are recently produced by nanotechnology that can significantly improve properties of materials compared with those of conventional ones, and which employs physical or chemical techniques to construct materials on a nanometre scale. This remarkable properties improvement is attributed to the significant increase in the fibre's boundary area or its functional surface. By nanotechnology new materials such as nanofibres, nanocomposites and nanocoated textiles are created (Gowri et al., 2010; Lin &Wang, 2009).

2.1 Nanofibres

Polymer nanofibres are produced by the electrospinning process, which uses electrical forces for creation of polymer fibres with nanometre-scale diameters. Electrospinning is a simple and relatively inexpensive method of producing nanofibres by solidification of a polymer solution or melt. By the fibre process formation the electrical forces at the surface of a polymer solution or melt overcome the surface tension and this phenomenon gives rise to the charged polymer jet to be released. Dried or solidified polymer jet is stretched by an electric field. In comparison to conventional fibre production methods electrospun fibres are much finer and fibre assemblies can form different nonwoven structures (Teo & Ramakrishna, 2006).

This technique enables production of various nanofibres from polymers, polymer blends and polymer composites to ceramics. Various synthetic and natural biodegradable polymers have been electrospun into fibres with diameters in the nanometre range. The nanofibre diameter, structure and physical properties can be effectively modified by controlling various parameters of the electrospinning process. Therefore a lot of research has been performed to study the influence of production parameters, e.g. solution concentration, tipto-collector distance, and the feed rate in producing nonwovens composed of different size fibres (Zhang et al., 2009).

Processing parameter effects on the internal molecular structure of electrospun semicrystalline PLLA fibres were investigated by Inai et al. It was found that take-up velocity is a dominant parameter to induce a highly ordered molecular structure in fibres compared to solution conductivity and polymer concentration. The last two parameters were important in controlling the fibre diameter. Due to the ordered structure of the fibres produced by higher take-up velocity their tensile modulus and strength were higher (Inai et al., 2005).

In spite of intensive research activities on interdependences between electrospinning production parameters and fibres finenesses and diameter variations which are the two most important nanofibres properties, the physical and mathematical descriptions of the electrospinning process are still not unambiguously defined therefore additional techniques , e.g. multiple regression analysis are used to study the process. From the results it is evident that polymer concentration and feed rate have significant and controlled impacts on creation of fibres with diameters in the nano-range and by these two parameters fibres diameter could be foreseen (Patra et al., 2010).

Despite the fact that the most of the studies and manufacturing processes were performed for electrospinning procedure of polymer solutions, spinning from polymer melts has a number of advantages and is also possible. Different polymers melts and solutions are appropriate for nanospinning, e.g. polyethylene oxide, polyamide PA, polyamide PA 6 blends, polyimide, DNA, aramid and polyaniline, etc (Reneker & Chun, 1996; Malakhov et al., 2009).

In addition to, PAN nanofibres were prepared via an electrospinning process. Fibres were not obtained in the electrospinning process when the polymer concentration was very low, however as the concentration increased, the fibre morphology changed from a beads structure to the fibre structure with increasing fibre diameters. The addition of a cationic surfactant positively influenced the fibre formation. The effect of polymer concentration on the fibre morphology was studied by Lin et al. (Lin et al., 2005).

The same observations were made for Poly(vinyl alcohol) (PVA) nanofibres which were obtained by electrospinning of PVA in water solutions. Formation of beaded structures combined with decreased fibre diameters was observed for low PVA concentrations. Fibres with higher fineness and more uniform diameter were obtained by spinning blends of PVA of different molecular weight when compared to the fibres spun from homopolymers of similar viscosity (Zhang et al., 2005).

The process of electrospinning of ultra fine PVA fibres which have potential applications in filtration and biomedical engineering was optimised by investigating the effects of various variables such as electric voltage, tip to target distance, flow rate and solution parameters on the morphology of nanofibres (Samani et al., 2009).

Additionally a theoretical analysis of the distribution of the electrostatic field forming around spinning points in the area where polymer streams are formed and stretched was performed by Krucinska et al. (Krucinska et al. 2009).

Due to some problems related to electrospinning technique such as low production rate, capillary clogging, etc. in recent years, several new electrospinning methods have been developed to solve these problems, e.g. by using multiple jets the production is increased.

Morphology of poly(vinyl alcohol) (PVA) electrospun fibres with inserted drugs, like Aspirin etc. was investigated by Zhang with co-workers. Fibres were prepared by electrospinning of PVA aqueous solutions. The researchers found out that the morphology of fibres was conditioned by the amount of drug, i.e. irregularly shaped fibres were formed with increasing drug amounts. However when comparing drug release from PVA nanofibres and PVA film, the release form nanofibres is more efficient due to the large surface area and high porosity of the electrospun fibre mats (Zhang et al., 2005).

Furthermore, it was detected that the morphology of the drug-loaded electrospun PVA mats depended on the nature of the incorporated drug. Drugs molecular weight has influenced inverse proportionally both, the rate and the total amount of drugs released from the drug-loaded electrospun PVA material (Taepaiboon et al., 2006).

Excellent physical properties such as high surface area, high porosity, interconnective pores of the nanofibre matrices and appropriate mechanical properties, well-controlled degradation rates and biocompatibility of the base polymer, make biodegradable polymeric nanofibre matrices ideal materials for developing scaffolds for tissue engineering (Nair et al., 2004).

To achieve additional functionalities of nanofibers, not only pure polymers, but their polymer blends were electrospun as well. By the procedure of bicomponent electrospinning nanoporous polyacrilonitrile fibres can be obtained, therefore polyacrylonitrile (PAN) and poly(ethylene oxide) (PEO) bicomponent fibres were spun and upon removal of the phase-separated PEO domains, became nanoporous. The nanoporous fibres generated from 50/50 PAN/PEO bicomponent precursor contained internal pores of a few nanometres to tens of

nanometres in size and had 50% higher pore volume and 2.5-times higher specific surface (Zhang & Hsieh, 2006).

Several bio-polymers were electrospun recently. Experimental attempts were made to fabricate man-made silk fibres by means of electrospinning and the properties of electrospun fibres were compared to the fibres obtained by wet spinning and dry spinning (Fu et al., 2009).

There were attempts to apply cellulose of different molecular weights from solutions of lithium chloride and N,N-dimethylacetamide (DMAc) and water solution of N-methylmorpholine N-oxide (NMNO), respectively for ellectrospinning procedure. Due to low efficiency some modifications of the process were suggested (heated solvents, etc). However the most efficient way to produce cellulose nanofibers is by electrospinning cellulose acetate (CA) followed by alkaline hydrolysis to revert the acetyl to hydroxyl groups (Du & Hsieh, 2009).

Cellulose acetate (CA) nanofibres mats were produced by dissolving CA in different solvents mixtures (ketones-acetone, methyl ethyl ketone (MEK), and alcohols-benzyl alcohol, propylene glycol and dimethylsulphoxide) and the process was optimized with the aim to produce uniform nanofibres (Haas et al., 2010).

Tissue engineering scaffolds produced by electrospinning are a very interesting research topic; therefore a lot of biocompatible polymers were introduced for their production. Some of them are: cellulose, chitosan, PVA, poly(E-caprolactone) (PCL)/hydroxyapatite (HA), etc. (Zargarian & Haddadi, 2010; Du & Hsieh, 2009; Sajeev et al., 2008).

Chitosan and gelatine as well as PVA have been widely used materials in recent years because of their excellent biocompatibility, biodegradability, bacteriostasis and other excellent characteristics. PVA/chitosan and PVA/gelatin nanofibrous composite membranes were fabricated using the electrospinning technique and the morphology of the fibres was observed to compare the spinnability of PVA/chitosan and PVA/gelatin electrospun fibres. Both materials exhibit good spinnability (Huang et al., 2009).

As chitin is characterised by limited processing possibilities, a chitin derivative has been developed, e.g. dibutyrylchitin, which is an ester chitin derivative and which can be easily dissolved in common solvents. A new method of manufacturing nonwoven products made from dibutyrylchitin for biomaterials was developed by Blasinska (Blasinska et al., 2004).

Nano-fibres containing quaternised chitosan (QCh) have been successfully prepared by electrospinning of QCh solutions mixed with poly(vinyl alcohol) (PVA). The obtained nano-fibrous electrospun mats are promising for wound-heating applications (Ignatova et al., 2006).

Electrospinning process is likewise appropriate for nanocomposites perparation. A lot of research was performed in studying the spinning conditions, the distribution of nanoparticles inside polymer, the polymer crystalline structure formation, interdependence of procedure conditions and structure morphology (Adomaviciene et al., 2010; Kim et al., 2007).

Different polymers and different fillers were used for nanocomposites preparation. Multiwall carbon nanotubes (MWCNT) were introduced into the bamboo cellulose matrix to form composite nanofibres by the liquid crystal electrospinning process (Wan & Ko, 2009); and in addition to, in silk fibroin (Bombyx mori) by dissolving regenerated silk fibroin and MWCNT in formic acid for electrospinning process (Kang et al., 2009).

Electrospun membranes based on nanofibres are used in a variety of applications, including filtration systems, tissue engineering and regenerative medicine, etc. Due to the interdisciplinary fields of their application the characterisation of the material is very

specific. Nisbet with co-authors reviewed the current status of the characterisation of electrospun membranes and pointed out deficiencies (Nisbet et al., 2009).

2.2 Nanofilled fibres

Several different nanoparticles for nanofilled composites, e.g. layered silicates (Benetti et al., 2005; Manias et al., 2001; Filho et al., 2005; Ray& Okamoto, 2003; Alexandre et al., 2002; Han et al., 2003; Tang et al., 2003), silica nanoparticles (Jain et al., 2005; Rong et al., 2001), carbon black (Horrocks et al. 1999; Jakab & Omastova, 2005) carbon nanotubes (Chatterjee & Deopura, 2006; Kearns & Shambaugh, 2002) metal containing nanoparticles (Gubin, 2002), elastomeric nanoparticles (Zhang et al, 2002), TiO₂ (Marcinčin et al., 2009) etc., have been reported.

The incorporation of one-, two- and three-dimensional nanoparticles, e.g. layered clays (Manias 2000; Marcinčin et al., 2008; Sfiligoj et al. 2009) nano-tubes (Chatterjee & Deopura, 2006; Kearns & Shambaugh, 2002), nanofibres (Hine et al., 2005, Li et al., 2004) metal containing nano-particles (Gubin, 2002), carbon black (Horrocks et al. 1999; Jakab & Omastova, 2005), etc. is used to prepare nanocomposite fibres.

For ultraviolet (UV) protection materials PP TiO_2 nanocomposite fibres were developed by Erdem. Filaments were melt spun from master batches of PP and 0.3, 1, and 3% TiO_2 nanoparticles, respectively which were prepared by melt compounding before spinning. Nanocomposites' mechanical properties were slightly affected by the addition of nanoparticles however the filaments exhibited excellent UV protection (Erdem et al., 2010).

By addition of nanoparticles to the spinning polymer melt or solution new fibres functionalities are obtained, however the procedure of spinning is thereby more complicated and it is often difficult to reach suitable spinning conditions. It is sometimes easier and more advantageous to functionalize textiles by subsequent nano-treatment.

2.3 Nanocoated fibres

Comprehensive research activities in the textile nanotechnology science are directed to enhance or/and impart new functionalities to textiles, i.e. improved abrasion and thermal properties (Cireli et al., 2007; Satoh et al., 2004; Hribernik et al., 2007), various repellent properties (water, oil, soil) (Pinto et al., 2008), easy to clean properties, protective properties, e.g. UV and EMR shielding (Xin et al., 2004; Onar et al., 2007; Abidi et al., 2007), electrical conductivity, antimicrobial activity (Gao & Cranston, 2008; Xu et al., 2006; Tarimala et al., 2006), etc. Nanocoatings of fibres offer excellent possibilities therefore (Wei et al., 2004; Mahltig et al., 2005; Sawhney et al., 2008).

To prepare nanocoated textiles there are mainly two distinct methodologies: deposition of morphological well-defined nanoparticles at the fibres surfaces or in situ synthesis of nanoparticles on fibres. For the lattermost procedure the sol-gel method is often used. By the sol-gel processing precursor solutions undergo gelation, aging and drying. By controlling the synthesis conditions carefully, these reactions may lead to a variety of structures, and to different final states of the material.

Several authors reported of SiO_2 nanocoated textiles obtained via sol-gel process according to the method developed by Stöber (Stöber et al., 1968). By this method spherical and monodisperse silica nano particles are grown however the coating morphology is determined by the reaction conditions, e.g. alkaline or acid catalysis, etc. Different precursors for the sol-gel processing of silicates are used, e.g. TMOS (tetramethoxysilane; Si

 $(OCH_3)_4$, TEOS (tetraethoxysilane; Si $(OCH_2CH_3)_4$). SiO₂ nanocoatings via tetraethoxysilane (TEOS) hydrolysis were prepared on different textile substrates (Li et al., 2008; Hribernik et al., 2007, Pinto et al., 2008; etc.). Silica particles were coated on carbon fabrics for enlargement of fibres surface roughness to enhance hydrophobicity on the basis of lotus leaf effect (Hsieh et al., 2008).

Modified silica nanocoatings make additional functionalities possible. Water repellent textiles via coating with various modified silica sols were prepared by Mahltig. Pure and with 3-glycidoxypropyl triethoxysilane co-condensed sols were modified by addition of alkyltrialkoxysilane, polysiloxane derivatives and a fluorine containing silane. The coatings were applied on polyester and polyamide/cotton blends (Mahltig & Böttcher, 2003). Yu et al. developed a water repellent coating for cotton fibres by applying silica nano particles and perfluorooctylated quaternary ammonium silane coupling agent (PFSC). Oil repellent properties of silica particles/PFSC treated cotton fabrics were also improved (Yu et al., 2007). The same effect was achieved by treating cotton fabrics by a combination of silicon precursor TEOS and fluorocarbon polymer (Yeh et al., 2007). The significant enhancement of superoleophobicity by the deposition of silica nanoparticles with a thin fluorination coating on the surface of the particles is attributed to the following facts: (i) surface fluorination (impact on surface tension), (ii) surface topography (roughness), and (iii) creation of bionic surface hierarchically combined with nano/submicron architecture (Hsieh et al., 2010). Gonçalves has prepared superhydrophobic cellulose nano composites by employing amorphous silica particles as a mean to enhance surface roughness and perfluoro moieties for reduction of surface energy. Resultant water contact angles approached a value of 150° (Gonçalves et al., 2008).

Silane agents which are often used in the nanocoating process for modifying fibres functionalities can form surface films on fibres and silica particles (Vanblaaderen & Vrij, 1993; Tomšič et al., 2007) or can be used as coupling agents between the fibres and silica particles.

Silica has served as well as a carrier for incorporation of dye-stuffs. Cheng et al. have prepared dye-containing silica sol-covered wool fabrics. Photocromic dyes were able to provide a very fast response to UV light (Cheng et al., 2007). Mahltig et al. have incorporated dyes into sol-gel coatings on textile fibres to develop a "one-type" recipe for dyeing different kinds of fabrics (Mahltig et al., 2004).

Nano-sized zinc oxide (ZnO) and more frequently titanium dioxide (TiO₂) particles are used for surface modification of different types of fibres for imparting the stain-release function. The ZnO nanoparticles were produced at different thermal conditions and media (water or 1,2-ethanediol) by Kathirvelu et al. A high temperature was necessary to obtain small monodispersed particles, which were then applied to cotton and polyester – cotton blend samples for achieving self-cleaning activity (Kathirvelu et al., 2010).

Numerous literature reports on the fabrication of TiO₂ thin films by sol-gel dip coating technique using many types of titanium alkoxides as precursors (Hamid & Rahman, 2003; Chrysicopoulou et al., 1998]; titanium tetraethoxide (Harizanov & Harizanova, 2000); titanium ethoxide (Ozer et al., 1995); titanium propoxide [Bell et al., 1994]; tetraisopropylorthotitanate (Su&Lu, 1998; Kajihara et al., 1998; Zaharescu et al., 1998; Avellaneda &Pawlicka., 1998); titanium tetra-n-butoxide (Imao et al., 2006). Others (Phani et al., 2002; Wang et al., 2002) have used titanium butoxide as starting materials for making TiO₂ thin films. Much work has been carried out depositing TiO_2 on heat resistant surfaces like glass, ceramics and silica by sol-gel methods, where temperatures up to 500 °C can be used. Several reports on TiO_2 application in the textile industry can be found as well (e.g. Bozzi et al., 2005a, b,; Daoud & Xin 2004; Veronovski et.al., 2006; Qi et al., 2007; Textor et al., 2007).

To obtain homogeneous TiO_2 nanocoatings and to investigate their self-cleaning effects when applied on cellulose materials Veronovski studied different procedures of nanocoating preparation. Several different approaches for achieving nanocoatings were used. First, coatings were generated in situ through an acid and alkaline catalyzed sol-gel process with or without added water. Titanium isopropoxide, TIP was used as TiO_2 precursor. Another type of coatings was prepared by using commercial TiO_2 P25 nanoparticles with good photocatalytic efficiency towards a broad range of organic pollutants and which is containing a mixture of rutile and anatase crystalline forms (Veronovski et al., 2006; Veronovski et al., 2009 a, b; Veronovski et al., 2010 a, b, c, d). $TiO_2 P$ 25 was used for textile nanocoatings preparation by other researchers as well (Bozzi et al., 2005 a, b; Daoud & Xin, 2004; Qi et al., 2007; Texlor et al., 2007).

In addition, nano-TiO₂ added in the wrinkle-resistant treatment of cotton fabric could act as a multi-functional finishing agent to improve the UV protection property (Lam et al., 2010).

Composite titania (TiO₂) and silica (SiO₂) coatings are used to prevent fibres from photooxidative damages. Titanium-silica mixed oxides can be produced by different processes (Doolin, et al., 1994; Nakabayashi, 1992; Reddy et al., 1993; Stakheev et al., 1993; Hung & Katz, 1992; Greegor et al., 1983), but the most common way is the sol-gel method (Imamura et al., 1996; Klein et al., 1996; Liu & Davis, 1994; Dagan et al., 1995; Dutoit et al., 1996; 1995; Walther et al., 1991). The conditions of the sol-gel process have the major influence on the properties of titanium-silica mixed oxides.

A TiO₂-SiO₂ coating on regenerated cellulose fibers was prepared using TiO₂ P25 nanoparticles and the sol-gel process for SiO₂ formation from tetraethoxysilane (TEOS) as the precursor (Veronovski et al., 2010 d). In addition to, pure TiO₂ P25 nanocoated fibres were prepared and the properties of modified fibres were compared. Both TiO₂ nanocoated surfaces demonstrated photocatalytic activity, however, better results were obtained when the surface was treated in TiO₂ P25 nanoparticles dispersion only. In the case of TiO₂-SiO₂ coating, TiO₂ activity was reduced due to SiO₂ film partially covering TiO₂ particles (Veronovski et al., 2010 d).

In addition to, TiO_2 was used to prepare ultraviolet resistant cotton fabrics. UV Protection Factor UPF 50+ values were measured for the TiO_2 -coated samples. Further it was found that the rutile phase was better than anatase phase in blocking UV rays. Modified textiles were compared to ZnO nanocoated cotton yarns, were the modification efficiency was not so high (Paul et al., 2010).

Photocatalytic self-cleaning TiO_2 nanocoatings were used for wool fibers modification by Wing. The process of sol-gel TiO_2 nanocoating formation was studied to prevent chemical damages and photo-degradation of wool fibres during the process. The sols were prepared using different catalysts, and media, for the hydrolysis and condensation reactions of the titanium dioxide precursor (Wing & Walid, 2009).

3. Electrokinetic effects

When two phases are placed in contact there develops, in general, a difference in potential between them. If one of the phases is a polar liquid, like water, its (dipolar) molecules will

tend to be oriented in a particular direction at the interface and this will generate a potential difference. If the surface of phase I is positively charged, its electrostatic potential will be positive with respect to the bulk of phase II; if phase II is a liquid containing dissolved ions, then as one moves from the surface into phase II, the potential will decrease, more or less regularly, until it becomes constant in the bulk liquid far from the surface of the phase I. The region where the liquid has a positive electrostatic potential will accumulate an excess of negative ions and repel positive ions of the electrolyte. It is this excess of negative ions which gradually lowers the electrostatic potential to zero in the bulk electrolyte. The arrangement of charges on the surface of the phase I and the charges in the liquid phase II is referred to as the electrical double layer at the interface. By the relative motion between an electrolyte and a charged solid surface (phase I, and II) a number of phenomena which are known as electrokinetic effects are observed. There are four distinct effects depending on the way in which motion is induced. They are: (i) electrophoresis, (ii) electro-osmosis, (iii) streaming potential and (iv) sedimentation potential (Hunter 1981; Jacobasch et al. 1995; Delgado et al. 2005; Reischel et al. 2008).

electrokinetic effect	measured	entity, that moves	Movement is
	quantity		caused by
electrophoresis	velocity	moving particles	electrical field
electro-osmosis	velocity	moving liquid through	electrical field
		the capillaries	
streaming potential	potential	moving liquid	pressure difference
sedimentation potential	potential	moving particles	gravitation

Table 1. The principles of electrokinetic effects

Electrophoresis: when a solid or liquid phase is suspended in liquid or gas phase, then a movement of particles can be induced with electrical field in the system. This phenomenon is called electrophoresis. Measurement of the particles' velocity in known external electrical field yields information on total charge of particles or their surface potential, related to the surrounding phase.

Electro-osmosis: the effect is known as electro-osmosis in a case of a non-moving solid phase and a moving liquid phase as a result of an electrical field. It's encountered with solid phases as capillaries or porous plugs, filled with liquid. Electrical field moves the ions of the liquid and therefore the liquid itself. Information is gained on the total surface charge or electrical potential near the surface.

Streaming potential: in this case, movement of liquid is caused by a pressure difference. Excess of charge near the surface is moving along with the liquid phase and the accumulation of charge causes the development of electric field with an opposite direction to that of the liquid. Measurement of the potential difference of the capillary or a porous plug is called streaming potential.

Sedimentation potential: when charged colloidal particles are moving in the liquid as a result of the gravitation or centrifuge field, potential difference occurs. Sedimentation potential is an electrical voltage, which is a result of charged particles' movement. Negative particles create negative field in the direction of movement, while equilibrium is achieved with a flow of positive ions in the opposite direction.

Different models of a charged surface, needed for the evaluation of the electrokinetic surface phenomena, have been developed over the years, however Gouy-Chapman-Stern-Graham model. GCSG is regarded as the most exact one, taking into account various different phenomena occurring in the polymer/electrolyte system and is as such most used in the modern evaluation of the charged surfaces.

3.1 Models of electrically charged surfaces in electrolyte solutions 3.1.1 Helmholtz - Perrin model

Helmholtz and Perrin developed a model which predicts the adsorption of oppositely charged ions from the electrolyte solutions onto a surface. Plane condenser is formed, therefore implying a linear electrical potential (ψ) in the adsorbed layer (Helmholtz layer) on the surface. Charges on the surface itself do not influence the electrolyte solution, since they are completely screened by the adsorbed layer of opposite charges. This model gave rise to the term double layer, which refers to the charges on the surface and charges from the electrolyte solution. Helmholtz - Perrin model does not take into account the structure of water or solvent, only the ions, present in the solution and also neglects their size and adsorption ability – rather, they are treated as point-like species, adsorbed to the surface via electrostatic interactions without taking into account other interactions.

3.1.2 Gouy - Chapman model

Gouy - Chapman model, developed after the Helmholtz - Perrin model, discards the notion of adsorbed charges on the surfaces, but rather predicts the position of ions along the surface according to the Boltzmann distribution. This implies a larger quantity of oppositely charged ions in the vicinity of the surface, while the difference in concentrations between different ions diminishes when moving further away from the surface. In this proposition, the double layer consists of charges on the surface and charges in the electrolyte solution; layer of ions at the surface is called diffuse layer, due to the mobility of the ions. Fall of the electrical potential with the distance from the surface is exponential within the diffuse layer. While Helmholtz - Perrin model neglected the thermal movement of ions in the solution, Gouy - Chapman model takes into account only thermal movement (Boltzmann distribution) and neglects the possibility that some charge may be adsorbed onto the surface – either in a fixed manner or in a form of dynamic equilibrium of constant exchange of electrolyte ions and adsorbed ions.

3.1.3 Stern model

Stern model is a combination of Helmholtz - Perrin model and Gouy - Chapman model. The most important aspects of Stern model are: ions are no longer treated as point-like species but are given some finite dimensions and they can adsorb onto a surface also via nonelectrostatic interactions (e.g. disperse interactions between ions and the charged surface). Since ions are not point-like, they find themselves adsorbed farther away from the surface than it was predicted in the Helmholtz - Perrin model. The fall of electric potential within this adsorbed layer is linear, but the surface charge is not completely screened by the adsorbed ions. The remaining part of the charge, needed for the complete screening of charged surface, is positioned in the diffuse layer, as previously postulated by the Gouy - Chapman model: ions in the diffuse layer are subjected to thermal movement and therefore Boltzmann distribution, while electrical potential falls exponentially. Important finding, derived from the Stern model is, that ions, which screen the surface charge can be situated either within the adsorbed layer (in this case the Stern layer) or in the diffuse layer. Amount of charge in both layers is influenced by the properties of electrolyte solution, that is, valence of ions and their concentration. In diluted solutions, most of the charge will be situated in the diffuse layer, while in concentrated solutions the majority of charge will be found in the Stern layer.

3.1.4 Gouy - Chapman - Stern - Graham model (GCSG model)

This model is considered as one of the most advanced, and is frequently encountered when dealing with charged surfaces in the electrolyte solutions. It differentiates itself from the Stern model by taking into account properties and structure of the water molecules in the solution. Stern layer is therefore divided into two parts, that is, inner Helmholtz plane and outer Helmholtz plane. Inner Helmholtz plane (IHP) is composed of a monolayer of water molecules adjacent to the surface, which are, due to the charged surface, ordered in such a way, that the lowest possible interaction energy exists between them and the surface. Water molecules at the surface are oriented as dipoles, in regard to the sign of the surface charge; when a surface is positively charged, water molecules are oriented toward the surface with their oxygen atoms, while in the case of a negative charge, they position themselves with hydrogen atoms to the surface. IHP also contains ions with a higher degree of mobility, which makes them preferentially adsorbed via dispersion forces. Since GCSG model takes into account the structure of water, the hydration state of ions is predicted - ions are surrounded with water molecules. Cations are more hydrated than anions, which is a result of a steric effect, since water molecules orient themselves with oxygen adjacent to them. Anions are therefore less limited in mobility, since a lesser amount of water molecules is attached to them, while in some cases, they are not hydrated at all. This is the reason for preferential adsorption of anions in the IHP, regardless of the sign of the charge on the surface - this preferential adsorption is also termed hydrophobic interaction.

As far as outer Helmholtz plane (OHP) is concerned, it is actually a Stern layer, composed of adsorbed ions, which are opposite in sign to that on the surface.

The most important aspect of the GCSG model is the recognition of the preferential adsorption of anions into IHP, even when the surface is negatively charged. This clearly implies, that other interactions are present, alongside the electrostatic ones.

3.2 Zeta potential

The zeta potential (ζ) is the term describing the electrokinetic properties at that position of the solid/liquid interface, which is accessible for interactions. This interface is described by chemical and electrochemical potential values different from those of the bulk phases since the molecules in the boundary are subject to interaction forces from both adjacent phases. The resulting net charge of the solid surfaceaqueous solution interfaces is generally attributed to different mechanisms. This is the dissociation of functional surface groups on one hand, and on the other hand the preferential adsorption of potential determining ions and other charged species from solution.

For the calculation of (ζ) potentials from streaming potential measurements, which is a common method for determination of fibres' zeta potential, the approach of Smoluchowski is used. It relates the (ζ) potential to the streaming potential/pressure gradient, the electrical

resistance over the sample, the viscosity of the electrolyte solution, and geometrical factors relating to the streaming channel for the electrolyte solution.

$$\zeta = \frac{U_s}{\Delta p} \frac{\eta}{\varepsilon_r \varepsilon_o} \frac{L}{Q} \frac{1}{R}$$
(1)

Here, U_s is the streaming potential, Δp is the applied pressure difference, η is the viscosity of the solution, $\varepsilon_r \varepsilon_0$ is the permittivity of the liquid medium, L is the streaming channel length, Q is the cross-sectional area of the streaming channel, and R is the electrical resistivity over the sample. This equation holds as long as the curvature of the measured system is sufficiently large ($\kappa a >>1$, where κ is the reciprocal Debye length and a is the curvature of the system). In addition, surface conductance and polarization of the electrical double layer is neglected.

Overbeek showed that the considerations for the streaming channel can also be extended to porous sample plugs, forming microchannels for the electrolyte flow. The channel geometry and sample resistivity can then be treated according to Fairbrother and Mastin (Fairbrother & Mastin 1924).

$$\frac{L}{Q} = \frac{R_s \chi_b}{R} \tag{2}$$

where R_S is the resistivity of the electrolyte solution and χ_b is the electrolyte conductivity. By substitution of Eq. 1 with Eq. 2, the ζ potential can be expressed as follows:

$$\zeta = \frac{U_s \eta \chi_b}{\Delta p \varepsilon_r \varepsilon_o} \tag{3}$$

A more general approach to the ζ potential equation is given in the following expression (Equation 4). Here, also the surface conductivity of the sample χ_s is accounted for.

$$\zeta = \frac{U_s \eta [\chi_b + f \chi_s]}{\Delta p \varepsilon_r \varepsilon_o} \tag{4}$$

The term f is called the form factor of the streaming channel. This equation can be used, if the surface conductivity of the sample is nonzero. If the surface conductivity is neglected ($\chi_s = 0$), then Equation 4 reduces to Equation 3.

4. Electrokinetic properties of nanocomposite fibres

4.1 Zeta potential of PP nanocomposite fibres

PP-based nanocomposite fibres were prepared by direct polymer melt intercalation and the electrokinetic properties of nannofilled fibres were measured (Župerl 2004, Sfiligoj et al. 2009). Fibres were spun from an isotactic iPP homopolymer (with MFI = 11g/10min - 16 g/10min and isotactic index 96 % (m/m)) with addition of polypropylene grafted with acrylic acid PPAA as a coupling agent. 10% and 20% of PPAA co-polymer, respectively were added. Montmorillonite (organoclay) MMT modified by N,N-dimethyl-N,N dioctadecylammonium

cations (Nanofil 15 from Südchemie, Germany) was used to prepare nanocomposite fibres with 0.5, 1 and 2 % of MMT, respectively. The melt spinning and in-line drawing of PP filaments was carried out (Župerl et al. 2002). The same spinning conditions were used for neat PP fibres, PP copolymer and MMT modified fibres.

To study electrokinetic properties the streaming potential method was used. The method is in detail described in e.g. Stana & Ribitsch 1998, Ribitsch & Stana 1998, Stana et al. 1999, Stana et al. 2001, Smole et al. 2002, etc.

 ζ was calculated from the streaming potential (U_s) data by use of the Smoluchowski equation (1) and Fairbrother and Mastin (FM) approach (2), in which the term (L/Q) is replaced by ($R_s \chi_b$), where R_s is the electrical resistance of the plug when the measurement cell is filled with an electrolyte with accurately known specific conductance χ_b .

Streaming potential measurements of fibres were performed on the Electrokinetic Analyzer EKA, A. Paar KG in the fibre cell using 0.001n KCl as electrolyte solution.

Electrokinetic properties of neat PP and PP fibers with added MMT, PP/ PPAA fibers and PP/ PPAA fibres modified with 0.5, 1 and 2% MMT, respectively were compared. Functional dependence pH/ zeta potential (ZP) for fibres spinned from neat PP homopolymer is demonstaretd in Figure 1.



Fig. 1. pH/ ζ diagram for PP homopolymer (x), PP/PPAA co-polymer (+) and PP nannocomposite fibres (\circ), rerspectively

Due to the PP non-polar chemical structure a typical non-polar pH/ ζ diagram is obtained. It demonstrates fibres' hydrophobe character with negative zeta potential value ZP at – 25 mV measured at pH=9 and an isoelectric point IE at pH = 3.5. By addition of PPAA (20%) ZP decreases to -51.5mV at pH=9, however only a slight shift of the isoelectric point towards acid region is observed (IE at pH =3.11). For PP nanocomposite fibres containing different amounts of MMT a reduction of zeta potential value and a slight shift of IE point towards neutral region is observed when compared to unmodified PP fibres. For the sample spinned from PP, PPAA (20%) and MMT (2%) the ZP was -32,8 at pH=9 and IE = 3.68. Although electrokinetic properties of nanocomposite fibres are conditioned by both influences; i.e. PPAA and MMT, nevertheless, the ζ -pH function results indicate that the electrokinetic surface properties are dominated by the PPAA containing dissociable carboxyl groups (Sfiligoj et al. 2009).

4.2 Zeta potential of nanocoated fibres

In addition to, we prepared SiO_2 nano coatings on different fibre types and their zeta potential was determined to study the electrokinetic properties and the influence of the coating morphology on zeta potential.



Fig. 2. SiO₂ nanocoated PET fibres (a) and regenerated cellulose fibres Modal (b) and Viscose (c) according to the procedure B

 SiO_2 is an important technical material which is often used in pharmaceutical industry and in production of catalysts and pigments, etc. Properties of materials containing SiO_2 particles are above all influenced by particles size and particles size distribution. There are two procedures of sol-gel particles preparation, (i.e. alkaline and acid) known from the literature. They both enable preparation of spherical SiO_2 particles in the range between 10 nm to some μ m.

In the research we prepared alkaline catalysed particles. The method is based on controlled hydrolysis of alkyl silicate and alcohol, followed by condensation of the dispersed phase. The procedure is known as the Stöber method. Particles size is conditioned by the type and mass share of alkyl silicate, NH_3 and H_2O , type and mass share of alcohol as the reaction medium and reaction temperature.

Nanocoatings were prepared by the sol-gel process from Tetraethylorthosilicat TEOS as precursor. To obtain different coatings morphologies process conditions were varied, i.e. different concentration of precursor, TEOS (0,2 and 0,5 mol/L), and catalyst NH₃ (0,3 and 0,5 mol/L) and two solvents (ethanol, propanol) were used. Different modification procedures were used and different fibre types were studied; i.e. cotton, regenerated cellulose fibres and polyethylene terephtalate PET. Prior to the modification fibres were pre-treated for 30

minutes in a solution of a non-ionic washing agent (1g/L) and in the case of cellulose fibres in 0.1 M HCl, respectively followed by washing in distilled water to the constant conductivity ($\leq 5 \mu$ S/cm).

Nanocoatings were prepared in propanol with 0.2 mol/L TEOS (procedure A) and with 0.5 mol/L TEOS (procedure B), in ethanol with 0.2 mol/L TEOS (procedure C) and with 0.5 mol/L TEOS (procedure D), respectively on different fibre types and SEM images of surface morphologies of some modified fibres prepared according to the modification procedure B are demonstrated in Figure 2.

Zeta potential – pH electrolyte functions of cellulose; i.e. natural cellulose cotton fibres (Fig. 3) and regenerated cellulose fibres Modal and Viscose, respectively and of SiO_2 modified fibres are demonstrated on Figures 4 -5.



(R-cotton fibre, RA-nanocoated cotton fibres by using procedure A, RB- nanocoated cotton fibres by using procedure B, RC- nanocoated cotton fibres by using procedure C, RD- nanocoated cotton fibres by using procedure D)

Fig. 3. Zeta potential of unmodified cotton fibre and nanocoated fibres as a function of pH



(M-Modal fibre, MA-nanocoated Modal fibres by using procedure A, MB- nanocoated Modal fibres by using procedure B, MC- nanocoated modal fibres by using procedure C, MD- nanocoated Modal fibres by using procedure D)

Fig. 4. Zeta potential of unmodified Modal fibre and nanocoated fibres as a function of pH

In addition to fibres with self-cleaning properties based on photocatalytic nano TiO_2 particles were prepared. For the nanomodification regenerated cellulose fibres Lyocell were

involved. Two different coatings types were created, i.e. TiO_2 and $TiO_2 - SiO_2$ nanocoating by using TiO_2 P25 nanoparticles (Degussa). TiO_2 P25 particles contain anatase and rutile phases in a ratio of about 3: 1. The average sizes of the anatase and rutile elementary particles are 85 and 25 nm, respectively (Ohno et al. 2001). After fibres pre-treatment Lyocell fibres were treated in a dispersion of 5 g/L TiO₂ P25 nanoparticles in deionised water at T = 60°C for 1 hour. For TiO₂-SiO₂ coating preparation, 0.5 mol/L TEOS as a precursor in the presence of ethanol as a solvent and 0.5 mol/L ammonia solution as a catalyst were added to the pre-dispersed aqueous solution of TiO₂ P25 nanoparticles at pH 5.39. Lyocell fibres were treated in the dispersion for 1 hour at elevated temperature (T = 60° C) (Veronovski et al. 2010d). Before measuring zeta potential of the modified fibres, nonadsorbed particles were removed by fibres' rinsing at pH 6.31 and heat treated for 15 minutes and additionally washed in an ultrasound bath for 5 minutes. Coatings morphologies are demonstrated in Fig. 6 and zeta potentials as a function of pH for untreated and coated fibre samples in Fig. 7.



(V-Viscose fibre, VA-nanocoated Viscose fibres by using procedure A, VB- nanocoated Viscose fibres by using procedure B, VC- nanocoated Viscose fibres by using procedure C, VD- nanocoated Viscose fibres by using procedure D)

Fig. 5. Zeta potential of unmodified Viscose fibre and nanocoated fibres as a function of pH



Fig. 6. SEM images of $TiO_2(a)$ and $TiO_2 - SiO_2(b)$ nanocoated Lyocell fibres

Natural cellulose fibres are negatively charged ($\zeta pH=9=-11 \text{ mV}$) due to the presence of carboxyl and hydroxyl-groups. In the case of raw (untreated) fibres these groups are covered by noncellulose compounds present in the primary wall of cotton fibre. Regenerated cellulose fibres are also negatively charged and their zeta potential is negative through the whole pH region, however zeta potential value is not the same for different types of regenerated cellulose fibres. It is well known that different production processes for regenerated cellulose fibres (Viscose, Modal, Lyocell) cause differences in their structure and in the reactivity – adsorption character of fibres despite having the same chemical composition. Lyocell fibres posses more ordered structure with higher crystallinity and higher molecular orientation when compared to Viscose and Modal fibres. The pore system of Viscose and Lyocell fibres is very similar and more comprehensive than the pore system in Modal fibres. These differences in the molecular and fine structure between various types of regenerated cellulose fibres cause different reactivity, sorption and electrokinetic properties (Stana-Kleinschek et al 2001). $\zeta_{\text{oH=9}} = -6.3 \text{ mV}$ for untreated Lyocell fibres, $\zeta_{pH=9} = -3$ mV for Viscose and $\zeta_{pH=9} = -9$ mV for Modal fibres. We can conclude that the highest negative zeta potential in the alkaline region was determined for Modal fibres and the lowest for Viscose probably due to the distinctions between the accessibility's of reactive groups (OH and COOH).

The adsorption of nanoparticles on cellulose fibres can be qualitatively confirmed by measuring the streaming potential of the samples as the introduction of nano groups significantly influences the ζ_{p} - pH diagram. The negative zeta potential is additionally decreased by nano SiO₂ coating. There are some differences in zeta potential according the coating procedure which was used.

In Figure 7 the zeta potential as a function of pH for untreated Lyocell and TiO₂ and TiO₂-SiO₂ coated fibres is presented. The typical diagram for a cellulose fibre with a negative zeta potential value through the whole pH region is changed by nanomodification; i.e. zeta potential values are increased. For the TiO₂ coated sample the zeta potential at pH =9 is -4.4 mV and for TiO₂-SiO₂ coated sample – 5.3 mV, respectively. The appearance of the isoelectric point in the diagram of nanocoated samples confirms the adsorption of nanoparticles. It is well known that the isoelectric point (IEP) of TiO₂ is in the range of pH 4.5–5, and in the case of SiO₂ particles, at pH 2 (Veronovski et al. 2010). The IEP of TiO₂-coated Lyocell fibre is at pH 3.55 and it shifts to pH = 2.75 when silica particles are covering TiO₂ particles.



(untreated Lyocell fibres, TiO₂ nanocoated Lyocel fibres and TiO₂ - SiO₂ nanocoated Lyocel fibres) Fig. 7. Zeta potential of unmodified Lyocell fibre and nanocoated fibres as a function of pH


(PET-polyethylene terephthalate fibre, PETA-nanocoated polyethylene terephthalate fibres by using procedure A, PETB- nanocoated polyethylene terephthalate fibres by using procedure B, PETC- nanocoated polyethylene terephthalate fibres by using procedure C, PETD- nanocoated polyethylene terephthalate fibres by using procedure D)

Fig. 8. Zeta potential of unmodified PET fibre and SiO₂ nanocoated fibres as a function of pH

The zeta potential at pH=9 ($\zeta_{pH=9}$) of unmodified PET fibres is app. -50 mV and the IEP at pH =3 (Fig.8) and significant changes of the zeta potential – pH functions are observed by SiO₂ nanocoating. Zeta potential values are changed conditioned by the modification procedure, however the IEP in not influenced by the treatment.

5. Conclusion

Improvement of existing properties and the creation of new material properties are the most important reasons for the functionalization of textiles. To design these additional materials properties nanotechnology is recently used. Nanocoating and inclusion of nanoparticles into fibres represent modification techniques with great potential for synthesis of novel functional materials however these technologies are still inadequately employed in the textile production.

The influence of nanomodification on surface properties of different fibre types can be studied by determination of zeta (ζ) potential as a function of pH. Based on functional dependence ζ =f (pH) we can conclude about acid – alkaline character of functional groups on fibres' surface and accessibility of these groups. ζ -potential of fibres surface is not only a parameter of quantity and type of dissociable species and adsorbed charged molecules or ions; but by measuring ζ -potential the hydrophilic /hydrophobic character of fibres and structural changes on fibres' surface can be valued.

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Designing of Nano Composites of Conducting Polymers for EMI Shielding

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1. Introduction

Enormous progress in nanotechnology has made electronic systems smaller and has increased the density of electrical components within an instrument. The operating frequencies of signals in these systems are also increasing and have created a new kind of problem called electromagnetic interference (EMI). To provide an adequate solution for the EMI problem, the shielding or absorbing of the electromagnetic field is taken into account. It is observed that the high conductivity and dielectric constant of the materials contribute to high EMI shielding efficiency (SE). This article is an evaluation of the ferrite based conducting polymer nanocomposite and underlines the complex interplay of its intrinsic properties with EMI shielding. The unique properties of nanostructured ferrite offer excellent prospects for designing a new kind of shielding materials. The absorption loss in the material is caused by the heat loss under the action between electric dipole and/or magnetic dipole in the shielding material and the electromagnetic field so that the absorption loss is the function of conductivity and the magnetic permeability of the material. The designing of ferrite based conducting polymer nanocomposites increases the shielding effectiveness. Conducting and magnetic properties of conducing polymer-ferrite nanocomposites can be tuned by suitable selection of polymerization conditions and controlled addition of ferrite nanoparticles. The contribution to the absorption value comes mainly due the magnetic losses (μ) and dielectric losses (ϵ). The dependence of SE_A on magnetic permeability and conductivity demonstrates that better absorption value has been obtained for material with higher conductivity and magnetization. Therefore, it has been concluded that the incorporation of magnetic and dielectric fillers in the polymer matrix lead to better absorbing material which make them futuristic radar absorbing material. This chapter examines the development of ferromagnetic conducting polymer nanocomposite in the context of its application as microwave absorber and concludes with some observations.

1.1 Conducting polymer-ferrite nanocomposites

Nature has mastered the use of nanocomposites, and researchers, as usual, are learning from their natural surroundings. In 1998, Chemistry in Britain published an article titled 'Nano sandwiches' [1], stating, 'Nature is a master chemist with incredible talent'. Using natural reagents and polymers such as carbohydrates, lipids, and proteins, nature makes strong composites such as bones, shells, and wood. These are examples of nanocomposites, made

by mixing two or more phases such as particles, layers or fibers, where at least one of the phases is in the 1-100nm size range. A nanocomposite is defined as a material with more than one solid phase, metal ceramic, or polymer, compositionally or structurally where at least one dimension falls in the nanometers range. Many composite materials are composed of just two phases; one is termed the matrix, which is continuous and surrounds the other phase, often called the dispersed phase. The properties of composites are a function of the properties of the constituent phases, their relative amounts, and the geometry of the dispersed phase. There have been great effort to fabricate nanocomposite to obtain unique physical properties since these properties become increasingly size dependent at low dimension. The combination of the nanomaterial with polymer is very attractive not only to reinforce polymer but also to introduce new electronic properties based on the morphological modification or electronic interaction between the two components. The properties of a nanocomposite are greatly influenced by the size scale of its component phases and the degree of mixing between the two phases. Depending on the nature of the components used and the method of preparation, significant differences in composite properties may be obtained. Nanocomposites of conducting polymers have been prepared by various methods such as colloidal dispersions [2], electrochemical encapsulation [3], coating of inorganic polymers, and insitu polymerization with nanoparticles [4] and have opened new avenues for material synthesis.

The combination of the magnetic nanoparticles with conducting polymer leads to formation of ferromagnetic conducting polymer composite possessing unique combination of both electrical and magnetic properties. This property of the nanocomposite can be used an electromagnetic shielding material since the electromagnetic wave consist of an electric (E) and the magnetic field (H) right angle to each other. The ratio over E to H factor (impedance) has been subjugated in the shielding purpose. The conducting ferromagnetic type of materials can effectively shield electromagnetic waves generated from an electric source, whereas electromagnetic waves from a magnetic source can be effectively shielded only by magnetic materials. The primary mechanism of EMI shielding is usually reflection. For reflection of the radiation by the shield, the shield must have mobile charge carriers (electrons or holes) which interact with the electromagnetic fields in the radiation. As a result, the shield tends to be electrically conducting, although a high conductivity is not required. For example, a volume resistivity in the order of 1 Ω cm is typically sufficient. A secondary mechanism of EMI shielding is usually absorption. For significant absorption of the radiation, the shield should have electric and/or magnetic dipoles which interact with the electromagnetic fields in the radiation. Thus, having both conducting and magnetic components in a single system could be used as an EMI shielding material.

The electrical permittivity $\varepsilon(\omega)$ and the magnetic permeability $\mu(\omega)$, depending upon the pulsation (ω =2πf), are the major physical parameters that characterize the material as a microwave absorber. It has been shown recently that promising shielding performance could be achieved with composites comprising of an electrically non-conducting polymer matrix filled with conducting objects such as CNT-polymer composites, nickel ceramic composites etc. [5-7]. However, high filler contents are required from 10-15% for fibers and 30% for spheres to reach a percolation level leading to microwave losses. These materials are generally compared to each other with respect to their imaginary part of permittivity (ε ") or loss tangent (ε "/ ε ') [8-10]. The design of large bandwidth structures requires multilayer structures in which the frequency behavior of these two parameters must be controlled [11-12]. Despite the large number of conductive fillers, the radio electric properties of all these

composites are generally same. Differences are due to the processing of the fillers in the matrix. They are often correlated with aggregation effects and inter-particle contacts processing of the fillers in the matrix. They are often correlated with aggregation effects and inter-particle contacts.

Nevertheless, the use of dielectric materials obtained by conductive filler dispersion (carbon black, graphite fibers, metallic powders) is limited. As a matter of fact, material performances are dependent on the filler content as well as particle aggregation phenomena [13-17]. These composites require a high level of reproducibility and their behavior is linked to the control of electronic inter-particle transfer. The measured parameter (complex permittivity) depends on the texture of the percolation aggregates and consequently on the processing conditions. The percolation threshold depends on the particle shape (sphere, plates or fibers). This filler aggregation during the processing, observed with nanometric particles (carbon black) or micron sized fillers (metallic or carbon sphere), leads to a very difficult reproducibility of the material. Different approaches have been proposed to overcome these drawbacks.

In this respect, conducting polymers represent a very attractive solution to the problem described above. These new materials present very promising properties because of the chemical nature of the macromolecular chains in which electronic conduction occurs at long range. These conducting polymers have some specific characteristics that make them far more interesting than traditional dielectric materials. Besides their reproducible properties, the chemistry of conducting polymers offers a great variety of methods of synthesis. The insertion of conductivity into various materials (insulating polymer matrix, reinforcing fabrics, honeycomb structure) is now possible which leads to complex structures [18-20].

They absorb radar waves and can match new environmental constraints (mechanical properties for example). The driving idea is based on the growing process at molecular scale of the conducting entity leading to a uniform macroscopic network in the material. Polyaniline, polypyrrole or polythiophene possess this property. Work has to be done to reach the compromise between compatibility of the conducting polymers and its processing properties. In particular, dependence of their conductivity on frequency, many ideas have been attempted to adapt these phenomenon to microwave applications [21-23]. The intrinsic conductivity of conjugated polymers in the field of microwave absorption (100MHz-20GHz) makes them viable materials.

1.2 Conducting polymers

Conducting polymer are highly delocalized π -electron system with alternate single and double bonds in the polymer backbone. The π -conjugation of the polymer chain generates high energy occupied molecular orbitals and low energy unoccupied molecular orbitals leading to a system that can be readily oxidized or reduced [24]. In 1977 Heeger, MacDiarmid and Shirakawa showed that polyacetylene, which is the simplest polyconjugated system, can be made conductive by reaction with bromine or iodine vapors. Spectroscopic studies, that followed demonstrated without any ambiguity that this reaction is redox in nature and consists of the transformation of neutral polymer chains into polycarbocations with simultaneous insertion of the corresponding number of Br₃⁻ or I₃⁻ anions between the polymer chains in order to neutralize the positive charge generated on the polymer chain. This important discovery initiated an extensive and systematic research of various aspects of the chemistry and physics of conjugated polymers both in their neutral (undoped) and charged (doped) states.



Fig. 1. Chemical structure of some undoped conjugated polymers

In most of the cases, polymers are insulators in their neutral state and they become conducting only after introduction of electron acceptors/donors by a process known as 'doping'. The conductivity of a polymer can be tuned by chemical manipulation such as the nature of the dopant, the degree of doping and blending with other polymers. Figure 1 shows the chemical structure of conjugated polymers in their neutral insulating state. Undoped conjugated polymers are semiconductors with band gaps ranging from 1 to 4eV, therefore their room temperature conductivities are very low, typically of the order of 10⁻⁸ S/cm or lower. However, doping can leads to an increase in conductivity of polymer by many orders of magnitude [25].

The concept of doping is unique and distinguishes conducting polymers from all other types of polymers [26, 27]. During the doping process, an undoped conjugated polymer having small conductivity, typically in the range of 10^{-10} to 10^{-5} S/cm, is converted to a doped conducting polymer, which is in 'metallic' conducting regime (1–10⁴ S/cm). The highest value reported to date has been obtained in iodine-doped polyacetylene (>10⁵ S/cm) and the predicted theoretical limit is about 2 × 10⁷, more than an order of magnitude higher than that of copper. Conductivity of other conjugated polymers reaches up to 10³ S/cm as shown in Figure 2. Recent advances in the field of intrinsic conducting polymers (ICPs) have led to a variety of materials with great potential for commercial applications such as rechargeable batteries [28-30],

1.3 Mechanism of conductivity

Conducting polymers are unusual in that they do not conduct electrons via the same mechanisms used to describe classical semiconductors and hence their electronic properties cannot be explained well by standard band theory. The electronic conductivity of conducting polymers results from mobile charge carriers introduced into the conjugated IIsystem through doping.

To explain the electronic phenomena in these organic conducting polymers, new concepts including solitons, polarons and bipolarons [31-35] have been proposed by solid-state physicists. The electronic structures of π -conjugated polymers with degenerate and non-degenerate ground states are different.



Fig. 2. Conductivity of some metals and doped conjugated polymers

In π -conjugated polymers with degenerate ground states, solitons are the important and dominant charge storage species. Polyacetylene, $(CH)_{x}$, is the only known polymer with a degenerate ground state due to its access to two possible configurations as shown in Figure 3 The two structures differ from each other by the position of carbon–carbon single and double bonds. While polyacetylene can exist in two isomeric forms: cis and transpolyacetylene, the trans-acetylene form is thermodynamically more stable and the cis–trans isomerization is irreversible [36].

A soliton can also be viewed as an excitation of the radical from one potential well to another well of the same energy (Figure 3 degenerate polyacetylene). A neutral soliton occurs in pristine trans-polyacetylene when a chain contains an odd number of conjugated carbons, in which case there remains an unpaired π -electron, a radical, which corresponds to a soliton (Figure 4). In a long chain, the spin density in a neutral soliton (or charge density in a charged soliton) is not localized on one carbon but spread over several carbons [36,37] which gives the soliton a width. Starting from one side of the soliton, the double bonds become gradually longer and the single bonds shorter, so that arriving at the other side, the alternation has completely reversed.



Fig. 3. Energetically equivalent forms of degenerated polyacetylene



Fig. 4. Top: schematic illustration of the geometric structure of a neutral soliton on a transpolyacetylene chain. Bottom: band structure for a transpolyacetylene chain containing a neutral soliton, positively charged soliton and negatively charged soliton.

This implies that the bond lengths do equalize in the middle of a soliton. The presence of a soliton leads to the appearance of a localized electronic level at mid-gap which is half occupied in the case of a neutral soliton and empty (doubly occupied) in the case of a positively (negatively) charged soliton (Figure 4). Similarly, in n-type doping, neutral chains are either chemically or electrochemically reduced to polycarbonium anions and simultaneously charged, spinless solitons are inserted into the polymer matrix. In this case, negatively charged, spinless solitons are charge carriers. Consider the structure of other conductive polymers such as poly-p-phenylene, polypyrrole and polyaniline. These polymers do not support soliton-like defects because the ground state energy of the quinoid form is substantially higher than the aromatic benzenoid structure figure, 5. As a result, the

charge defects on these polymers are different [38]. As an example, consider the oxidation of polypyrrole (Figure 6). Removal of an electron from a pyrrole unit leads to the formation of a polaron consisting of a tightly bound radical and cation. The binding arises from the increase in the energy (of the defect) with increasing radical-cation separation. The increase in energy is partly due to a loss of aromaticity.



Fig. 5. Resonance forms in conjugated polymers. The quinoid form has the higher energy than the benzenoid form.



Fig. 6. Polaron and bipolaron formation on π -conjugated backbone of polypyrrole or polythiophene

Calculations on polypyrrole and polythiophene indicate that two polarons in close proximity are unstable with respect to the formation of a bipolaron [39-41]. The two free radicals combine leaving behind two cations separated by a quinoidal section of the polymer chain. Figure 6 shows that the two cations have some freedom to separate. However, the higher energy of the quinoid section between them binds them together

resulting in correlated motion. The net effect is the formation of a doubly charged defect acting like a single entity and delocalized over several rings (3-5) i.e., a bipolaron.

The formation of bipolarons implies a net free energy gain in forming a closed shell defect from two open shell structures. The quinoid form has a higher energy than the aromatic benzenoid form but its electron affinity is higher and the ionization potential lower [41]. This leads to the formation of two localized states in the band gap. As the doping is increased, additional states are created in the gap and they finally evolve into two narrow bands.

The theoretically expected evolution of the electronic structure (e.g., for poly thiophene or polypyrrole) with doping is shown schematically in figure 7. At low doping levels, the defects are polarons, which tend to combine at higher doping levels to form bipolarons. The two bands inside the band gap are empty in the case of bipolarons while the lower polaron band is half-filled. Figure 7 also shows the optical transition characteristics of the charge defects. The bandgap transition W_o increases in energy with doping level because the interband states are derived from states at the band edges. Doping results in the appearance of mid-gap transitions. Three ingap transitions are characteristic of polaron states while bipolaron states are noted for the absence of the transition W₃. The evolution of the optical spectra with doping level provided experimental evidence for the picture presented in figure 7 for polypyrrole (PPy) and other polymers [41, 42]. At low doping levels, PPy shows the three interband transitions characteristic of polaron states. As the doping level is increased, the transition W_3 decreases in intensity and finally disappears. This behavior provides evidence for the formation of bipolarons in the polypyrrole chain. As an internal check for the assignment of transitions, note that the sum (in energy values) of W_1 and W_2 approximately add up to the interband transition W_o.



Fig. 7. Schematic representation of electronic structure on doping for polypyrrole or polythiophene

Let us now consider some peculiarities of the polyaniline system. In the conventional conductive polymers, e.g., polypyrrole, polythiophene, polyacetylene and poly-pphenylene, etc., oxidative doping results in the removal of electrons from the bonding π -system. In polyaniline, in contrast, the initial removal of electrons is from the non-bonding nitrogen lone pairs. Unlike other conducting polymers, the quinoid form is not just simply an alternative resonance form. Its formation requires reduction and deprotonation so that it actually differs in chemical composition from the benzenoid form (figure 5). This peculiarity of the polyaniline structure makes doping by an acid-base reaction (figure 8) possible. In addition, the constituent parts of both the polaron and the bipolaron are very tightly bound owing to valence restrictions. The radical cations of the polaron are confined to a single aniline residue. The bipolaron is confined to, and identical with a (doubly protonated) quinone-diimine unit. This narrow confinement may destabilize bipolarons with respect to polarons owing to the coulomb repulsion between the cations. As indicated above, doping of polyaniline can be achieved via two routes (see figure 8). Doping by oxidation of the leucoemeraldine form, results in the formation of radical cations which may then convert to bipolarons. Alternatively, protonation of the emeraldine base form leads to the initial formation of bipolarons that may rearrange with neutral amine units to form radical cations.



Fig. 8. Oxidative and protonic acid doping in the polyaniline system

1.4 Charge carrier transport

While the exact nature of the charge carriers in conductive polymers is uncertain, the physics of charge transport is controversial at best. This is especially true in view of the unexpectedly high conductivity, approaching that of copper, recently reported for polyacetylene [43]. For this reason, only a few basic concepts are presented here. The temperature dependence of conductivity will be emphasized as the distinguishing feature among these mechanisms. Admittedly, this is a somewhat naive approach since the temperature dependence may vary, for each model, under special circumstances. An example that comes to mind, is the T-1/4 dependence of ln(σ) in the localized Fermi glass model where T and σ represents the temperature and conductivity respectively. It gives way

to a T^{-1/2} law when the assumed smooth varying density of states function is replaced by one with a sharp minimum at the Fermi level [44].

It is possible to differentiate between intra- and intermolecular charge transport mechanisms in conducting polymers [45]. Charge may be delocalized along the polymer backbone but without an efficient intermolecular tunneling or hopping mechanism, conductivity may still be low. Since conducting polymers are generally refractory materials, poor inter particle contacts may further limit conductivity in compressed pellets. Unhomogeneous doping may also lead to a dependence on doping level, which does not reflect intrinsic behavior, but derives from the microscopic topology of the granular dispersion: The conductivity of a dispersion of conducting particles in an insulating matrix shows percolation effects [46]. The composite shows a dramatic rise in conductivity above a threshold loading corresponding to the formation of an 'infinite' network of particles in mutual contact. The complicating factor here is that differential thermal expansion coefficients may lead to pseudo temperature dependence.

In conductive polymers, soliton and polaron, or bipolaron states can overlap to form bands of states [47]. In principle, a metallic state may result when such bands are partially filled. Overlap of bipolaron bands with the valence band and a regular array of polarons [48] are examples of such metallic states with a finite density of states at the Fermi level. Historically, the concept of a metallic state for the conductive form of PANI was marked by revolutionary change (Figure 8). One of the initial suggestions by MacDiarmid [49] was that the metallic state in PANI derives from a delocalized bipolaron defect. On the other hand, Epstein and coworkers [50,51] favored a metallic state derived from a regular array of polarons (Figure 8). Since the observed temperature dependence for the conductivity is not metallic, they proposed a picture of metallic particles embedded in a dielectric medium. The conductivity of such a granular metal is determined by space charging limited tunneling. At low field strengths, the field dependence is Ohmic with the temperature dependence given by [52]

$$\sigma = \sigma_o \exp\left[-\left(\frac{T_o}{T}\right)^{1/2}\right] \tag{1}$$

While at high field strengths

$$\sigma = \sigma_o \exp\left(-\frac{E_o}{E}\right) \tag{2}$$

Wudl et al. [53] disagree with the proposed metallic nature for the conductive state in polyaniline. They argue that the relatively low conductivity and high concentration of Curie spins is inconsistent with a true metallic state. According to them, severe disorder in this system results in a continuous density of localized states. For this situation the Fermi glass model [54,55] provides a more appropriate description. The temperature dependence of the conductivity should then follow a T^{-1/4} law according to the Mott-Davis variable range hopping (VRH) model [43]

$$\sigma = AT^{-1/2} \exp\left[-\left(\frac{T_o}{T}\right)^{1/4}\right]$$
(3)

The multi phonon hopping mechanism for charge transfer between localized states proposed by Buhks et al. [56] predicts a temperature dependence of the form

$$\sigma = AT^{-3/2} \exp\left(-\frac{E_a}{KT}\right) \tag{4}$$

In this model, the charge-transfer reorganization energy is estimated from the Marcus relationship [57]. The Marcus equation was first developed for outer sphere electron transfer (redox reactions) in solution [58]. The reorganization energy is a linear function of the medium (solvent) parameter [59]

$$\tau = 1/n^2 - 1/\varepsilon \tag{5}$$

where n is the refractive index and ε is the dielectric constant. This suggests that absorbed solvent may influence the conductivity of electroactive polymers. Indeed, the sensitivity of polyaniline conductivity to moisture content is well known [60]. In the more localized models, charge transport occurs via hopping between localized states. Note that in polyacetylene hopping of a single soliton from one chain to another requires high reorganization energy. In contrast, the coordinated hopping of two defects (i.e. a bipolaron) is a low activation energy process. The situation is reversed in polyaniline. Hopping of a polaron requires a single electron transfer with minimal structural rearrangement [61], In PANI, hopping of bipolarons requires a higher activation energy since it involves considerable structural relaxation.

2. Electromagnetic shielding and microwave absorption

The term shielding is usually referred to a metallic enclosure that completely encloses an electronic product or the portion of that product. Therefore, it limits the amount of EMI radiation from the external environment that can penetrate the circuit and conversely, it influences how much EMI energy generated by the circuit can escape into the external environment. There are two functions of a shield: first, to prevent the emissions of the electronics of the product or a portion of those electronics from the radiation outside the boundaries of the product. The motivation here is to either prevent those emissions from causing the product to fail to comply with the radiated emissions limits or to prevent the product from causing interference with the other electronics products. The second purpose of the shield is, to prevent the radiated emission outside the product electronics that may cause interference in the product. Therefore, a shield is conceptually, a barrier to the transmission of the electromagnetic fields. We can say that the effectiveness of a shield as being the ratio of the magnitude of the electric (magnetic) field that is incident on the barrier.

If sensitive equipment is enclosed within a thin, conductive, spherical shell that is placed in an E-field, it will be shielded because the current setup by the electromagnetic wave does not conduct inside of the shell. This is not because the shell has completely absorbed the field but because the E-field has caused electronic charges of different polarity along the shell. These charges generate an electrical field that will tend to cancel the original field inside the shell [62,63]. The thickness of the shell can be very small when the wave frequency is high enough. The electromagnetic current takes the path of least-resistance and follows through the exterior of the conductive shell.

When it comes to H-fields, shields made of a soft magnetic material with high permeability, μ >>1, and sufficient thickness attenuate the magnetic field in the shielding shell by providing a low reluctance. That is, the spherical shell of magnetic material with good permeability will reduce the H-field intensity inside because the H-field tends to remain in the magnetic material layer as the magnetic material offers a low-reluctance path [62,64].

Alternatively, a thin shield made of a conductive material with low permeability can also provide effective shielding for H-fields at high frequencies. This is because an alternating H-field will induce eddy currents in the shielding screen, assuming that the shield has adequate conductivity. These eddy currents will themselves create an alternating H- field of the opposite orientation inside the shell. The effect will increase as the frequency increases, resulting in high shielding effectiveness at high frequencies. Therefore, it is relatively difficult to shield against low frequency H-fields. Magnetic absorption shielding typically needs the installation of thick shields constructed of expensive magnetic materials, conductive shields based on the induced current principle may be reasonably effective at power line frequencies. For example, aluminum screens are commonly used to protect against 50 and 60 Hz magnetic fields generated by transformers and other sources [62].

2.1 Shielding effectiveness

Shielding can be specified in the terms of reduction in magnetic (and electric) field or planewave strength caused by shielding. The effectiveness of a shield and its resulting EMI attenuation are based on the frequency, the distance of the shield from the source, the thickness of the shield and the shield material. Shielding effectiveness (SE) is normally expressed in decibels (dB) as a function of the logarithm of the ratio of the incident and exit electric (E), magnetic (H), or plane-wave field intensities (F): SE (dB) = 20 log (E_o/E_1), SE (dB) = 20 log (H_o/H_1), or SE (dB) = 20 log (F_o/F_1), respectively. With any kind of electromagnetic interference, there are three mechanisms contributing to the effectiveness of a shield. Part of the incident radiation is reflected from the front surface of the shield, part is absorbed within the shield material and part is reflected from the shield rear surface to the front where it can aid or hinder the effectiveness of the shield depending on its phase relationship with the incident wave, as shown in Figure 9.

Therefore, the total shielding effectiveness of a shielding material (SE) equals the sum of the absorption factor (SE_A), the reflection factor (SE_R) and the correction factor to account for multiple reflections (SE_M) in thin shields [65-68]

$$SE = SE_A + SE_R + SE_M$$
(6)

All the terms in the equation are expressed in dB. The multiple reflection factor SE_M , can be neglected if the absorption loss SE_A is greater than 10 dB. In practical calculation, SE_M can also be neglected for electric fields and plane waves.

2.1.1 Absorption loss

Absorption loss SE_A , is a function of the physical characteristics of the shield and is independent of the type of source field. Therefore, the absorption term SE_A is the same for all three waves. When an electromagnetic wave passes through a medium, its amplitude decreases exponentially, as shown in Figure 9. This decay or absorption loss occurs because currents induced in the medium produce ohmic losses and heating of the material, where E_1 and H_1 can be expressed as $E_1 = E_0 e^{-t/\delta}$ and $H_1 = H_0 e^{-t/\delta}$ [68]. The distance required by the wave to be attenuated to 1/e or 37% is defined as the skin depth. Therefore, the absorption term SE_A in decibel is given by the expression:

$$SE_{A} = 20(t/\delta)\log e = 8.69(t/\delta) = 131.t\sqrt{f\mu\sigma}$$
(7)

where, t is the thickness of the shield in mm; f is frequency in MHz; μ is relative permeability (1 for copper); σ is conductivity relative to copper. The skin depth δ can be expressed as:

$$\delta = \frac{1}{\sqrt{\pi f \mu \sigma}} \tag{8}$$

The absorption loss of one skin depth in a shield is approximately 9 dB. Skin effect is especially important at low frequencies, where the fields experienced are more likely to be predominantly magnetic with lower wave impedance than 377 Ω . From the absorption loss point of view, a good material for a shield will have high conductivity and high permeability along with a sufficient thickness to achieve the required number of skin depths at the lowest frequency of concern.



Fig. 9. Graphical representation of EMI shielding

2.1.2 Reflection loss

The reflection loss is related to the relative mismatch between the incident wave and the surface impedance of the shield. The computation of refection losses can be greatly simplified by considering shielding effectiveness for incident electric fields as a separate problem from that of electric, magnetic or plane waves. The equations for the three principle fields are given by the expressions [68]

$$R_E = K_1 10 \log\left(\frac{\sigma}{f^3 r^2 \mu}\right) \tag{9}$$

$$R_H = K_2 10 \log\left(\frac{fr^2\sigma}{\mu}\right) \tag{10}$$

$$R_P = K_3 10 \log\left(\frac{f\mu}{\sigma}\right) \tag{11}$$

where, R_E , R_H , and R_P are the reflection losses for the electric, magnetic and plane wave fields, respectively, expressed in dB; σ is the relative conductivity relative to copper; f is the frequency in Hz; μ is the relative permeability relative to free space; r is the distance from the source to the shielding in meter.

2.1.3 Multiple reflections

The factor SE_M can be mathematically positive or negative (in practice, it is always negative) and becomes insignificant when the absorption loss $SE_A > 6$ dB. It is usually only important when metals are thin and at low frequencies (i.e., below approximately 20 kHz). The formulation of factor SE_M can be expressed as

$$SE_M = -20\log(1 - e^{-2t/\delta})$$
 (12)

3. Theoretical calculations of shielding effectiveness

Calculation of the far-field shielding effectiveness (SE) of a planar barrier is a straightforward exercise in classical electromagnetic theory. It requires calculation of a solution of Maxwell's equations describing the decrease in amplitude of an electromagnetic disturbance that is produced by the presence of the shield of interest. To facilitate this calculation, it is most convenient to choose a field representation in terms of the electric and magnetic field strength vectors \vec{E} and \vec{H} . The components of these two vectors, which are tangential to the surface of the shield, are continuous across the interface between the shield's exterior and its interior.

The magnetic field strength is related to the magnetic induction \vec{B} through the empirical relation $\vec{B} = \mu \vec{H}$. A useful relation between \vec{E} and \vec{B} can be derived from Maxwell's equation for the Faraday law of induction which relates the spatial variation of \vec{E} to the temporal variation of \vec{B} :

$$\nabla \times \vec{E} = -\frac{\partial \vec{B}}{\partial t} \tag{13}$$

To generate an expression for the far-field SE of a planar barrier, consider a linearly polarized plane wave for which the variation in time and space of the vector fields \vec{E} and \vec{B} are expressed in the usual way:

$$\vec{E} = \vec{E}_o e^{i(\omega t \pm k.x)} \tag{14}$$

$$\vec{B} = \vec{B}_{o} e^{i(\omega t \pm k.x)} \tag{15}$$

(where, \vec{E}_o and \vec{B}_o are constant vectors giving the wave amplitude, ω is the angular frequency of the wave, $\vec{k} = \frac{2\pi}{\lambda}\hat{k}$, is the wave vector, and λ is its wavelength), then the differential equation (10) becomes the time-independent algebraic equation:

$$\mp i\vec{k}\times\vec{E} = -i\omega\mu\vec{H} \tag{16}$$

The vector equation (16) can be further simplified using the dispersion relation ω = ck and the relationship between the propagation velocity c and the constants ε and μ the electric permittivity and the magnetic permeability respectively, of the medium in which the wave propagates):

$$\vec{k} \times \vec{E} = \pm \frac{\omega \mu}{k} \vec{H} = \pm \frac{1}{\sqrt{\varepsilon \mu}} \mu \vec{H} = \pm \sqrt{\frac{\mu}{\varepsilon}} \vec{H} = \pm Z \vec{H}$$
(17)

The quantity $Z = \sqrt{\frac{\mu}{\varepsilon}}$ is the wave impedance in the medium of propagation. In the following discussion, the variable q is used to represent the magnitude of the wave vector in a conducting medium and k is used to represent the magnitude of the wave vector in free space. In terms of the conductivity σ of the medium, its relative permittivity ε_{r} , and its relative permeability μ_{r} , q is given by

$$q = \omega \left[\mu \left(\varepsilon - i \frac{\sigma}{\omega} \right) \right]^{1/2} = \frac{\omega}{c} \sqrt{\varepsilon_r \mu_r} \left[1 - i \frac{\sigma}{\omega \varepsilon} \right]^{1/2}$$
(18)

Hence, the complex wave function Z in the conducting medium can be written as

$$Z = \frac{\omega\mu}{q} = \frac{\mu}{\left[\mu\left(\varepsilon - i\frac{\sigma}{\omega}\right)\right]^{1/2}} = \sqrt{\frac{\mu}{\varepsilon}} \left[1 - i\frac{\sigma}{\omega\varepsilon}\right]^{-1/2}$$
(19)

Now, to calculate the far-field shielding of a thin sheet of a conducting material, assume that a plane wave linearly polarized in the y direction is incident from the -x direction onto a sheet of the conductor. The thickness of the sheet is denoted by d, and its orientation is assumed to be such that it lies in the y-z plane. If x increases from left to right, then to the left of the conducting sheet there is an incident wave with electric field strength $\vec{E}_o e^{-ikx}$ and a corresponding reflected wave $R\vec{E}_o e^{ikx}$ where the reflection amplitude R is, in general, a

complex number. To the right of the sheet there is a transmitted wave propagating in the x direction whose electric field strength can be written $T\vec{E}_{o}e^{-ikx}$. The shielding effectiveness of the sheet, in dB, is calculated from the (complex) transmission amplitude T according to the following expression:

$$SE(dB) = 10.\log\left(\frac{1}{\left|T\right|^2}\right)$$
(20)

Calculation of the transmission amplitude T is an elementary boundary value problem. Assuming that the electromagnetic disturbance within the sheet has an electric field strength with a spatial variation of the form $Ae^{-iqx} + Be^{iqx}$, the expressions representing the amplitudes of the standing electric and magnetic waves in each of the three regions (to the left of the shield, within the shield and to the right of the shield) are as shown in the schematic diagram below:



where, equation (17) has been used to express the magnetic field strength in terms of E_0 and the wave impedance. Continuity of the tangential component of \vec{E} across the left interface implies the equation:

$$E_o\left(e^{-ikx} + \operatorname{Re}^{ikx}\right) = Ae^{-iqx} + Be^{iqx}$$
⁽²¹⁾

Similarly, the continuity of the tangential component of \vec{H} yields the additional condition:

$$\frac{E_o}{Z_o} \left(e^{-ikx} - \operatorname{Re}^{ikx} \right) = \frac{1}{Z} \left(A e^{-iqx} - B e^{iqx} \right)$$
(22)

where, $Z_o = \sqrt{\frac{\mu_o}{\varepsilon_o}} = 377\Omega$ is the impedance of free space. Application of the boundary conditions at the right interface produces two additional equations:

$$Ae^{-iqx} + Be^{iqx} = TE_o e^{-ikx}$$
⁽²³⁾

$$\frac{1}{Z} \left(A e^{-iqx} - B e^{iqx} \right) = T \frac{E_o}{Z_o} e^{-ikx}$$
(24)

Now, taking the location of the left interface to be x = 0, equations (21) and (22) can be combined to give E_0 in terms of A and B:

$$E_{o} = \frac{1}{2} \left(1 + \frac{Z_{o}}{Z} \right) A + \frac{1}{2} \left(1 - \frac{Z_{o}}{Z} \right) B$$
(25)

Similarly, taking the location of the right interface to be x = d, (23) and (24) give expressions for A and B in terms of T and E₀:

$$A = \frac{1}{2} \left(1 + \frac{Z}{Z_o} \right) T E_o e^{-i(k-q)d}$$
⁽²⁶⁾

$$B = \frac{1}{2} \left(1 - \frac{Z}{Z_o} \right) T E_o e^{-i(k+q)d}$$
⁽²⁷⁾

After solving these equations and inserting the value of q, the transmission amplitude T can be written as

$$\frac{1}{|T|^2} = \frac{1}{4}\beta^2 \left[\cosh\left(\frac{2d}{\delta}\right) - \cos\left(\frac{2d}{\delta}\right) \right] + \frac{1}{2}\beta \left[\sinh\left(\frac{2d}{\delta}\right) + \sin\left(\frac{2d}{\delta}\right) \right] + \frac{1}{2} \left[\cosh\left(\frac{2d}{\delta}\right) + \cos\left(\frac{2d}{\delta}\right) \right]$$
(28)

This expression for the fractional transmitted intensity is very useful for the analysis of the experimentally measured far field SE of thin conductive polymer shields in the radio frequency and microwave regions of the electromagnetic spectrum. It has two interesting limits that physically correspond to the cases for which the thickness of the conducting sheet is greater or less than the classical skin depth δ . This is relevant to the materials of interest since, the skin depth (which decreases with increasing frequency like $\omega^{-1/2}$) at 100 MHz for a sheet of conductivity 0.1 S/cm is still about 2 cm - a bit larger than the thickness of a practical shield. At frequencies low enough, d << δ , (28) simplifies to:

$$\frac{1}{|T|^2} = \left(\frac{\beta d}{\delta}\right)^2 + 2\left(\frac{\beta d}{\delta}\right) + 1 = \left(\frac{\beta d}{\delta} + 1\right)^2 = \left(\frac{1}{2}Z_o d\sigma + 1\right)^2$$
(29)

Hence, the shielding effectiveness in the low frequency limit is frequency independent and is given by:

$$SE(dB) \approx 20.\log\left(1 + \frac{1}{2}Z_o d\sigma\right)$$
 (30)

Similarly, at the frequency high enough, $d >> \delta$, expression (28) can be written as

$$\frac{1}{\left|T\right|^{2}} \approx \frac{1}{8} \beta^{2} e^{2d/\delta} \tag{31}$$

leading to the following expression for the SE, which monotonically increases with frequency as a result of the dominance of the second term on the right hand side:

$$SE(dB) \approx 10.\log\left(\frac{\sigma}{16\omega\varepsilon}\right) + 20.\log e.d\sqrt{\frac{\omega\mu\sigma}{2}}$$
 (32)

The first term on the right hand side of this expression can be interpreted as due to reflection of the incident energy while, the second is attributable to attenuation of the incident wave by absorption in the bulk of the sheet. Equations (28) and (32) are plotted in the figure below for the frequency range from 1 MHz to 10 GHz. The sheet thickness d was taken to be 3 mm, and its conductivity σ is 3 S/cm. The upper solid curve represents the high frequency limit of the SE as given by equation (32) which is seen to converge to the actual far-field SE (calculated from the expression in equation (28) and represented below by the lower solid curve) at the frequency ω_c at which the skin depth δ is equal to the sheet thickness d. The two dashed curves shown represent the two terms on the right hand side of equation (32). The low frequency limit of the SE expressed in equation (30) corresponds to the frequency independent portion of the lower solid curve showing the actual far-field SE.



Fig. 10. Theoretical dependence of shielding effectiveness on frequency

In a straightforward way, the analysis of the shielding effectiveness of a thin planar barrier can be extended to an investigation of the effectiveness of two parallel planar barriers with a space between them. Depending on the particular values of the parameters describing this system (barrier thicknesses, inter-barrier spacing, barrier conductivity, signal frequency, etc.), the presence of the space between the barriers will produce interference effects which produce either an enhancement or suppression of the shielding effectiveness.

3.1 Calculations of complex permeability and permittivity

There are various approaches for obtaining the permittivity and permeability from sparameters. Table 1 gives an overview of the conversion techniques utilizing various sets of s-parameters to determine the dielectric properties. Each of the conversion technique has different advantages and limitations. The selection of the technique depends on several factors such as the measured s-parameters, sample length, the desired dielectric properties, speed of conversion and accuracies in the converted results. The details of these techniques are described below

Conversion technique	S-parameters	Dielectric properties
NRW	$(S_{11}, S_{21}, S_{12}, S_{22})$ or a pair (S_{11}, S_{21})	ϵ_r and μ_r
NIST iterative	$(S_{11}, S_{21}, S_{12}, S_{22})$ or a pair (S_{11}, S_{21})	ε_r and $\mu_r = 1$
New non-iterative	$(S_{11}, S_{21}, S_{12}, S_{22})$ or a pair (S_{11}, S_{21})	ε_r and $\mu_r = 1$
SCL	S ₁₁	ε _r

Table 1. Comparison between the conversion techniques

NRW method

Nicholson-Ross-Weir (NRW) technique provides a direct calculation of both the permittivity and permeability from the s-parameters [69-70]. It is the most commonly used technique for performing such conversions. Measurement of reflection coefficient and transmission coefficient requires all four (S_{11} , S_{21} , S_{12} , S_{22}) or a pair (S_{11} , S_{21}) of s-parameters of the material under test to be measured.

However, the technique diverges for low loss materials at frequencies corresponding to integer multiples of one-half wavelength in the sample which is due to the phase ambiguity. Hence, it is restricted to optimum sample thickness of $\lambda_g/4$ and used preferably for short samples

The procedure proposed by NRW method is deduced from the following equations:

$$S_{11} = \frac{\Gamma(1 - T^2)}{(1 - \Gamma^2 T^2)}$$
 and $S_{21} = \frac{T(1 - \Gamma_2)}{(1 - \Gamma_2 T_2)}$

These parameters can be obtained directly from the network analyzer. The reflection coefficient can be deduced as:

$$\Gamma = X \pm \sqrt{X^2 - 1} \tag{33}$$

where, $|\Gamma_1| < 1$ is required for finding the correct root and in terms of S-parameter

$$X = \frac{S_{11}^2 - S_{21}^2 + 1}{2S_{11}} \tag{34}$$

The transmission coefficient can be written as:

$$T = \frac{S_{11} + S_{21} - \Gamma}{1 - (S_{11} - S_{21})\Gamma}$$
(35)

The permeability is given as:

$$\mu_r = \frac{1 + \Gamma_1}{\Lambda (1 - \Gamma) \sqrt{\frac{1}{\lambda_o^2} - \frac{1}{\lambda_c^2}}}$$
(36)

where, λ_0 is the free space wavelength and λ_c is the cutoff wavelength and

$$\frac{1}{\Lambda^2} = \left(\frac{\varepsilon_r \mu_r}{\lambda_o^2} - \frac{1}{\lambda_c^2}\right) = -\left[\frac{1}{2\pi L} \ln\left(\frac{1}{T}\right)\right]^2$$
(37)

The permittivity can be defined as

$$\varepsilon_r = \frac{\lambda_o^2}{\mu_r} \left(\frac{1}{\lambda_c^2} - \left[\frac{1}{2\pi L} \ln\left(\frac{1}{T}\right) \right]^2 \right)$$
(38)

Equation (37) and (38) have an infinite number of roots since the imaginary part of the term ln(1/T) is equal to $i(\theta + 2\pi n)$ where, $n=0, \pm 1, \pm 2...$, the integer of (L/λ_g) . The n can be determined by two methods.

First method is by analysis of group delay and second is by estimating from λg using initial guess values of ϵ_r^* and μ_r^* for the sample. From the these methods the permittivity can be obtained as

$$\varepsilon_r = \mu_r \frac{\left(1 - \Gamma\right)^2}{\left(1 + \Gamma\right)^2} \left(1 - \frac{\lambda_o^2}{\lambda_c^2}\right) + \frac{\lambda_o^2}{\mu_r \lambda_c^2}$$
(39)

where, L = length of material ε_r = relative permittivity μ_r = relative permeability ε_r^* = initial guess permeability λ_g = wavelength in sample γ = propagation constant of material c = velocity of light f = frequency.

4. Synthesis of conducting ferromagnetic polyaniline-ferrite Composite

Generally polyaniline (PANI) is synthesized via chemical or electrochemical oxidation of a monomer where the polymerization reaction is stoichiometric in electrons. However, number of methods such as photochemical polymerization [71], pyrolysis [72,73], metal-catalyzed polymerization [74-76], solid-state polymerization [77], plasma polymerization [78], ring-forming condensation [79], step-growth polymerization [80, 81], and soluble precursor polymer preparation [82, 83], have been reported in literature for synthesis of conjugated polymers. Here only chemical and electrochemical polymerization are described briefly.

4.1 Chemical polymerization

Polyaniline (Different forms of polyaniline are shown in Figure 11) emeraldine salt can be easily obtained as dark green powder by polymerization of aniline in aqueous media using oxidizing agents such as ammonium persulfate. The main advantage of chemical synthesis is its ease and capability to produce large volumes of polyaniline in good yield. The reaction is mainly carried out in acid medium at pH between 0 and 2. The concentration of the monomer employed varies between 0.01 and 1 M. Generally, a stoichiometric equivalent of oxidant is used to avoid degradation of the polymer. Oxidative chemical polymerization is generally carried out at low temperatures (-15 to 5°C) in order to obtain polyaniline with high molecular weight.

4.2 Electrochemical polymerization

The anodic oxidation of aniline is generally carried out on an inert electrode material which is usually platinum. Polymerization of aniline is carried out in a three electrode single compartment containing aqueous acidic solution of aniline. The two commonly employed electrochemical routes are galvanostatic and potentiostatic modes. In the latter case, potential can be fixed (from 0.7 V to 1.2 V) or cycled (in the range of – 0.2 V to 0.9 V). The anodic oxidation is normally carried out in an inert atmosphere at ambient temperature. For many conceivable applications, deposition of the polymer as a thin film or thick coating is desirable which can be easily achieved using electrochemical polymerization.



Fig. 11. Different forms of polyaniline; leucoemeraldine (completely reduced polymer); emeraldine base (half-oxidized half-reduced polymer); pernigraniline (fully oxidized polymer)

4.3 Synthesis of conducting ferromagnetic nanocompositec by emulsion polymerization

Chemical oxidation of aniline in aqueous acidic media using ammonium persulfate oxidant is the most widely employed method [84, 85]. However, for the synthesis of ferrite

nanocomposite, the chemical oxidation of aniline in the presence of inorganic acid has some limitations like, dissociation of ferrite moieties at lower pH value and settling of ferrite particles due to higher density. Therefore, emulsion polymerization is an appropriate polymerization reaction which takes place in a large number of loci dispersed in a continuous external phase. Emulsion polymerization methods have several distinct advantages over the conventional in situ polymerization. The physical state of the emulsion system makes it easier to control the process. In a typical synthesis process, functional protonic acid such as dodecyl benzene sulphonic acid (DBSA) is used which being a bulky molecule, can act both as a surfactant and as dopant. Surfactants are amphiphilic compounds containing polar (hydrophilic) head and non-polar (hydrophobic) tails [86]. The polymerization of aniline monomer in the presence DBSA (dodecyl benzene sulfonic acid) leads to the formation of emeraldine salt form of polyaniline (figure 12). When the ferrite particles are homogenized with DBSA in aqueous solution, micelles are formed as surfactant form aggregates in which the hydrophobic tail are oriented towards the interior of the micelles leaving the hydrophilic group in contact with the aqueous medium [87]. In emulsion polymerization of intrinsic conducting polymers, the monomer and the ferrite particles assemble themselves in to micelles. The location of the monomer in the micelles is important as it can dictate the reaction mechanism and the properties of the final product [88]. The semipolar aniline monomer locates at the palisade layer (the region between the hydrophilic groups and the first few carbon atoms of the hydrophobic groups) of the micelle with the polar group at the micellar surface and the nonpolar hydrocarbon groups in the micellar. Anilinium cations sit between the individual DBSA molecules near the shell of the micelle complexed with sulfonate ion. When polymerization proceeds, anilinium cations are polymerized within the micelle together with DBSA and ferrite particles resulting in the formation of polyaniline-ferrite nanocomposites. Pictorial representation for the formation of polyaniline-ferrite composite is shown in figure13



Fig. 12. Schematic representation of the polymerization of aniline by formation of micelles

Polymerization methods generally play a very vital role in polymer morphology, internal structure, defects and degree of doping. Micro emulsion polymerization has very precise control over the properties of the polymer as it has high degree of polymerization then the normal suspension and precipitation method. In the polyaniline-DBSA formation in aqueous medium, water is the continuous phase and DBSA is a surfactant that acts as discontinuous phase. Monomer aniline is emulsified to form the micro micelles of oil in water type. Emulsion polymerization has high degree of polymerization than those prepared by suspension and precipitation method. A typical micelle in aqueous solution forms a roughly spherical or globular aggregate with the hydrophilic "head" regions in contact with surrounding solvent, sequestering the hydrophobic tail regions in the miccelle center.



Fig. 13. Pictorial representation for the formation of polyaniline –ferrite nanocomposite by chemical oxidative polymerization

The shape of a micelle is a function of the molecular geometry of its surfactant molecules and solution conditions such as surfactant concentration, temperature, pH and ionic strength. Generally, in micellar solution there are the chances of formation of macroscopic particles that can be prevented by adding the steric stabilizers like poly (vinyl alcohol), poly (N-vinylpyrrolidone) and cellulose ethers, but in this present system the bulky surfactant dodecyl benzene sulphonic acid itself acts to prevent the formation of the macroscopic precipitation. When monomer aniline is added to the DBSA micelle, it occupies the place in between the micelle and the hydrophilic sulphonate unit, subsequently on addition of oxidant like APS, the polymerization takes place at the interface boundary. When the oxidative polymerization of the micellar solution of aniline was carried out by using the ammonium peroxydisulphate, the color of the solution started changing from white to light green and finally to dark black green after the complete polymerization in eight hours. Addition of the APS to the aniline monomer leads to the formation of cation radicals which combine with another monomer moiety to form a dimer, which on further oxidation and combination with another cation radical forms a

termer and ultimately to a long chain of polymer. The schematic representation of the polymerization mechanism is shown in Figure 14.



Fig. 14. Polymerization mechanism of aniline using ammonium peroxydisulphate as oxidant

5. Characterization

5.1 X-ray diffraction studies

The X-ray diffraction patterns of barium ferrite, polyaniline doped with DBSA and its composites with different concentration of barium ferrite is shown in Figure 15. The main peaks of barium ferrite have been observed at 2θ ; 30.294° (d=2.9480), 32.14° (d=2.7827), 34.083° (d=2.6284), 37.046° (d=2.4247), 40.254° (d=2.2386), 42.391° (d=2.1305), 55.018° (d=1.6677), 56.477° (d=1.6280) and 63.054° (d=1.4731) corresponding to the (110), (107), (114), (203), (205), (206), (217), (2011) and (220) reflections, respectively. The peaks present in XRD-pattern of barium ferrite have also been observed in all the compositions of polyaniline composite with barium ferrite which indicates the presence of ferrite particles in the polymer matrix. With the increase in the concentration of ferrite particles in the polymer medium, the intensity of the peaks increases which shows the formation polymer composite with higher crystallinity. While the presence of polyaniline and its semi crystalline nature is confirmed by the broad peaks at 19.795° (d=4.481 Å) and 25.154° (d=3.537 Å), it is observed that the intensity of these peaks decreases with the increase in barium ferrite concentration in the composites. The crystallite size of barium ferrite particle can be calculated by line broadening using Scherrer's formula

$$D = \frac{k\lambda}{\beta\cos\theta} \tag{40}$$

where λ is the X-ray wavelength, k the shape factor, D is the crystallite size in angstroms, θ the Bragg angle in degrees, and β is the line broadening FWHM measured in radians. The value of k is often assigned as 0.89 which depends on several factors including the Miller

index of the reflecting plane and the shape of the crystal. The average crystallite size of barium ferrite particles has been calculated using above equation and estimated as 25 nm.



Fig. 15. X-ray diffraction plots of barium ferrite, PBF12, PBF11 and PD13



Fig. 16. (A) X-ray diffraction patterns of (a) BaF, (b) PEDOT-BaF12, (c) PEDOT-BaF11, (d) PEDOT-BaF21 and (e) PEDOT-DBSA. Plots b, c and d confirm the presence of barium ferrite in the polymer composites.

Figure 16 illustrates the X-ray diffraction patterns of PEDOT-DBSA, barium ferrite, PEDOT nanocomposites with different compositions of barium ferrite (PEDOT-BaF). PEDOT-DBSA shows two broad peaks at $2\theta = 19^{\circ}$ and 25° , which reveals its amorphous nature. With the addition of ferrite particle, the peaks of barium ferrite start appearing in the composite and and lead to enhanced crystallinity.

5.2 TEM & HRTEM analysis

TEM and HRTEM images of the barium ferrite and its polymer composites have been shown in figure 17. Figure 17b and 17c demonstrate that the barium ferrite nanoparticles synthesized by the precursor method have agglomerated morphology and found to be of cylindrical shape comprising of 50-70 nm diameter. The presence of ferrite phase in the polymer has also been confirmed by the EDS (Energy dispersive X-ray spectroscopy) as shown in figure 17d, which reveal the elemental signature of the polymer nanocomposite. HRTEM images (figure 17e & 17f) and electron diffraction (figure 17a) pattern of the polyaniline barium ferrite composites (PBF21) and (PBF12) show the presence of crystalline ferrite phase in volume of the polymer composites. The lattice fringes, corresponding to the (107) reflection, reveals the presence of polycrystalline barium ferrite phase. Inset to figure 17f show the fast fourier transform of the lattice fringes observed in the HRTEM image.



Fig. 17. (a) & (b) Transmission electron micrograph of barium ferrite nanoparticles, (c) Electron diffraction pattern of polyaniline barium ferrite composite with [aniline]/[Barium ferrite] ratio of 1:2(PBF12)(d) Energy dispersive X-ray spectroscopy pattern (EDS) of PBF12 and high resolution TEM image of (e) PBF21, inset shows the magnified image of the selected section (f) PBF12 and inset show the fast Fourier transform of the lattice fringes.
Figure 18 demonstrates the high-resolution transmission electron microscopy (HRTEM) images and energy dispersive x-ray spectroscopy (EDS) pattern of PEDOT-BaF nanocomposites. Figure 18a and 18b clearly indicates that the *in-situ* emulsion process leads to the formation of core-shell type morphology with ferrite particles as the center while the polymer (PEDOT) forms the outer covering of nanoparticles. The shell of the particle gives an impression of an amorphous layer as no fringes have been observed at the shell. The lattice plane spacing of the core ferrite particles is about 0.26 nm, which corresponds to the (1 1 4) plane of a barium ferrite phase (figure.18c). The elemental analysis of the composite has been performed using energy dispersive x-ray spectroscopy as shown in figure 18d. The peak of sulfur is due to the dopant DBSA while Cu and Si are the impressions of copper grid and the silicon detector. The presence of conducting shell encapsulating the magnetic and dielectric nanoparticles is helpful for the proper impedance matching which is necessary for enhancing the absorption of the electromagnetic wave.



Fig. 18. Low magnification HRTEM image of (a) PEDOT-barium ferrite composite having [EDOT]/[Barium ferrite] ratio of 1:2 (PEDOT-BaF12), (b) 1:1(PEDOT-BaF11) nanocomposites, showing the core-shell morphology. (c) High magnification HRTEM image of PEDOT-BaF12 showing the (114) oriented lattice planes of barium ferrite and (d) energy dispersive X-ray spectroscopy (EDS) pattern of PEDOT-BaF12

5.3 Thermo gravimetric analysis

The thermogravimetric analysis of polyaniline doped with dodecylbenzene sulfonic acid show that it is thermally stable up to 230°C which is much stable than the inorganic acid doped polyaniline like HCl (stable up to 150°C). Figure 19a shows the thermogram of different samples of polyaniline doped with different amount of DBSA. Thermogram of polymer shows

three major weight losses; initial weight loss at 100°C is attributed due to the loss of water contents. From 230-380°C is supposed to be due to the decomposition of DBSA from the polymer chain because, in case of undoped form of polyaniline no major step is observed in this temperature range. The degradation of the polymer chains starts at 400°C and continues up to 700°C. The extent of protonation can be estimated from the total amount of weight loss from the different samples. From the thermograms, it has been observed that the total weight loss increases as the concentration of the dopant DBSA increase.



Fig. 19a. Thermograms of polyaniline doped with [aniline]/[DBSA]molar ratio of 3:1(PD31), 2:1(PD21), 1:1(PD11), 1:2(PD12), 1:3(PD13) along with its undoped form (emeraldine base)



Fig. 19b. Thermo gravimetric analysis plots of polyaniline doped with DBSA and polyaniline-Barium ferrite composite having [aniline]/[barium ferrite] ratio of 2:1(PBF21), 1:1(PBF11), 1:2(PBF12) and 1:3(PBF13).

The effects of barium ferrite constituent on the thermal stability of the polyaniline-barium ferrite composites have shown in figure 19b. In the case polyaniline doped with DBSA (PD13), degradation of the polymer starts at 230°C due to the loss of DBSA from the polymer. However, when conducting polymer has been synthesized by incorporating ferrite moieties in the reaction system along with the surfactant, it has been observed that the thermal stability of the polymer has increased to 260°C. In case of PEDOT the Figure 20a demonstrates the effect of barium ferrite concentration on the thermal stability of PEDOT. On comparing the thermograms of PEDOT-Barium ferrite composites with the thermal behavior of the PEDOT-DBSA, the thermal stability of the composite has been found to increase up to 330°C. This increase in the thermal stability can be accounted to be due to the interaction of the barium ferrite with the sulfur atom of the thiophene ring.



Fig. 20. Thermo gravimetric analysis of (a) PEDOT-DBSA, PEDOT-barium ferrite composite having [EDOT]/[Barium ferrite] ratio of 1:1(PEDOT-BaF11) and 1:2 (PEDOT-BaF12) PEDOT-BaF21, PEDOT-BaF11 and PEDOT-BaF12 composites.

5.4 Magnetic studies

The magnetic properties of the polyaniline-barium ferrite composites (PBF) have been studied by the M-H hysteresis loop (figure 21). The saturation magnetization (M_s) value of the barium ferrite has been found to be 49emu/g at an external field of 8 kOe. When these nano ferrite particles have been incorporated in the polyaniline matrix, the saturation magnetization value varies as a function of ferrite concentration. M_s value for polyaniline-Barium ferrite composite having [aniline]/[Barium ferrite] ratio of 1:1(PBF11) has been found to be 14emu/g and it increases to 28emu/g with increase of ferrite content. The increase in saturation magnetization is due to the high poly-dispersivity of the barium ferrite in polyaniline matrix that arises due to the functionalization of nano ferrite particles with the surfactant DBSA.

The saturation magnetization (M_s) value of the barium ferrite has been found to be 54 emu/g at an external field of 8kGauss having coercivity value of 800 gauss and retentively value of 19.5 emu/g with a hysteresis loop, placing it in the category of hard ferrites. When these nano ferrite particles have been incorporated in the polymer matrix in weight ratio of 1:1 (PEDOT-BaF11), the saturation magnetization (M_s) value has been found to be 16.3emu/g. However, on changing the weight composition of [EDOT]/[BaF] to 1:2, the M_s has been increased from 16.3emu/g to 30.8emu/g, keeping the external applied field at 9kG (figure 22a). It has been observed that M_s increases with the ferrite content for the PEDOT-BaF composites which depends on the weight fraction of the magnetic barium ferrite. This

type of behavior has been observed in ferrites having high curie temperature and which have been cooled slowly which causes slight oxidation of the sample. The coercivity of the PEDOT- barium ferrite composites increases with the ferrite content. The barium ferrite particles embedded into PEDOT chains have an irregular structure, geometric and crystallographic nature, such as pores, cracks, surface roughness and impurities, the microstructure of the composites may lead to the variation of the coercivity. Furthermore, the coercivity is related to magnetic domain walls movement because the PEDOT chains are twisted which hinder the magnetic domain walls movement in the ferrite, resulting in increasing the coercivity of the samples. The observed hysteresis loop shows little variation from the regular magnetization curve of barium ferrite which may be attributed due to the annealing conditions and also to the increase in the iron concentration.



Fig. 21. Magnetization curves of barium ferrite, polyaniline-Barium ferrite composite having [aniline]/[Barium ferrite] ratio of 1:1(PBF11), 1:2(PBF12) and 1:3(PBF13).



Fig. 22. Magnetization curves of (a) barium ferrite, PEDOT-BaF21, PEDOT-BaF11, and PEDOT-BaF12

5.5 Shielding measurements

The EMI shielding effectiveness (SE) of a material is defined as the ratio of transmitted power to the incident power and given by

$$SE(dB) = -10\log\frac{P_t}{P_0} \tag{41}$$

where, P_t and P_0 are the transmitted and incident electromagnetic power, respectively. The amount of attenuation offered by the shield depends on three mechanisms. The first is usually a reflection of a wave from the shields, second is an absorption in to the shields as it passes through the shield and the third one is re-reflection, i.e., multiple reflections at various surface. For a shielding material, total SE is the sum SE_R + SE_A + SE_M, where, SE_R is due to reflection, SE_A is due to absorption and SE_M is due to multiple reflections [89].

In two-port network analyzer, S-parameters S_{11} (S_{22}) and S_{21} (S_{12}) represent the reflection and the transmission coefficients;

$$T = \left|\frac{E_T}{E_I}\right|^2 = \left|S_{21}\right|^2 = \left|S_{12}\right|^2 \tag{42}$$

$$R = \left|\frac{E_R}{E_I}\right|^2 = \left|S_{11}\right|^2 = \left|S_{22}\right|^2$$
(43)

$$A = 1 - R - T$$
 (44)

Here, it is noted that A is given with respect to the power of the incident EM wave. If the effect of multiple reflection between both interfaces of the material is negligible, the relative intensity of the effectively incident EM wave inside the material after reflection is based on the quantity 1-R. Therefore, the effective absorbance (A_{eff}) can be described as

$$A_{eff} = \frac{1 - R - T}{1 - R} \tag{45}$$

with respect to the power of the effectively incident EM wave inside the shielding material. It is convenient that reflectance and effective absorbance are expressed the form of $-10\log (1-R)$ and $-10\log (1-A_{\text{eff}})$ in decibel (dB), respectively, which provide the SE_A as follows:

$$SE_R = -10\log(1-R) \tag{46}$$

$$SE_A = -10\log(1 - A_{eff}) = -10\log\frac{T}{1 - R}$$
(47)

Figure 23 shows the shielding effectiveness of polyaniline doped with DBSA in the frequency range of 8.2 to 12.4 GHz. The SE_R and SE_A values have been calculated by using equation 46 and 47. It has been found that on increasing the DBSA concentration during the polymerization of aniline to polyaniline, the SE_R value decreases from 2.8 to 2.2dB while SE_A increases from 16.3 to 26.5dB calculated at 12.4 GHz. In conducting polymer the absorption part contributes more towards the shielding effectiveness as compared to reflection component which is just reverse of metallic material. Polyaniline with lower concentration

of dopant i.e. [aniline]/[DBDA] in ratio of 3:1 (PD31) has SE_R value of 2.8dB and SE_A value of 16.3dB whereas in ratio of 1:4 (PD14) shows smaller SE_R of the order of 2.2dB with higher SE_A value of the order of 26.5dB. This increase in the shielding effectiveness due to absorption is due to the increase in the conductivity of the polyaniline that leads to increase in the number of free charge carriers which results in higher polarizability and high ac conductivity. These results suggest that the microwave absorption loss in polyaniline depends upon concentration of dopant DBSA. In case of polyaniline-barium ferrite (PBF) nanocomposite (Figure 24) the shielding effectiveness (SE) mainly due to absorption and it is found to increase with ferrite concentration and it stabilizes after the threshold loading. The variation of SE_A for the composite having the [aniline] / [Barium ferrite] ratio of 2:1 (PBF21) has been found to be minimum (11.8dB to 13.8dB) whereas the composite with higher ratio for the 1:3 (PBF13), the SE_A has been found to be maximum (19.9dB to 28.9dB) while the SE due to reflection has been found to be nominal and its contribution is very little. The calculated value of SE_R lies between 1.8dB to 3.1dB.



Fig. 23. Variation of shielding effectiveness due to (a) reflection (SE_R) and (b) absorption (SE_A) in the frequency range of 8.2-12.4GHz of polyaniline having [aniline]/[DBSA] ratio of 3:1(PD31), 2:1(PD21), 1:1(PD11), 1:2(PD12), 1:3 (PD13, 1:4 (PD14.)

The effect of skin depth and AC conductivity on shielding effectiveness has been studied. For a material, the skin depth (δ) is the distance up to which the intensity of the electromagnetic wave decreases to 1/e of its original strength. The skin depth is related with the attenuation constant (β) of the wave propagation vector $\delta = 1/\beta = \sqrt{2/\omega\mu\sigma_{AC}}$ with the approximations that $\sigma >> \omega\epsilon$. As $\delta \propto \omega^{-1/2}$, therefore, at low frequencies, for electrically thin samples (d << δ), the shielding effectiveness of the sample is given as

SE (dB) =
$$20\log\left(1 + \frac{1}{2}Z_O d\sigma\right)$$
 (48)

where, σ is the ac conductivity, Z_o is free space impedance and d is the sample thickness. For the higher frequencies, sample thickness (electrically thick samples) is sufficiently greater than skin depth and EMI shielding effectiveness for the plane electromagnetic wave [90] is given by

$$SE (dB) = SE_R (dB) + SE_A (dB),$$
(49)

$$SE_R(dB) \approx 10\log\left(\frac{\sigma_{AC}}{16\omega\varepsilon_o\mu_r}\right)$$
, and (50)

$$SE_A(dB) = 20.\frac{d}{\delta}.\log e$$
 (51)

where, σ_{AC} depends upon the dielectric properties [91] ($\sigma_{AC} = \omega \varepsilon_0 \varepsilon''$) of the material, ω is the angular frequency (ω =2 π f), ε_0 is the free space permittivity and μ_r is the relative magnetic permeability of the sample. In equation 49, the first term is related to the reflection of the EM wave and contributes as the shielding effectiveness due to reflection. The second term expresses the loss due to the absorption of the wave when it passes through the shielding material. In microwave range, the contribution of the second part becomes more as compared to the reflection term.



Fig. 24. Dependence of shielding effectiveness (SE_A & SE_R) on frequency showing the effect of barium ferrite concentration on the SE_A value of the nanocomposites in the polyaniline-barium ferrite composite having aniline/[barium ferrite] ratio of 2:1(PBF21), 1:1(PBF11), 1:2(PBF12) and 1:3(PBF13).

It has been observed that SE_R increases with the increase in σ_{AC} and decreases with the increase in frequency and the permeability of the material as shown in figure 25a. Figure 25b shows that SE_A varies with the square root of conductivity whereas the variation of σ_{AC} and skin depth with frequency has been shown in the inset of figure 25a and 25b, respectively. It is also observed that with the increase of barium ferrite in the polymer matrix, σ_{AC} and μ_r increases which lead to higher shielding effectiveness of the composite.

In case of PEDOT composite, Figure 26 shows the variation of the shielding effectiveness with frequency for the different ratios of the [EDOT]/[BaF]. As compared to the lower SE of



Fig. 25. (a) Variation of SE_R as a function of log σ_{AC} while the inset shows the variation of σ_{AC} with the increase in frequency and (b) variation of SE_A as function of $(\sigma_{AC})^{1/2}$ while the inset shows the change in skin depth (δ) with the increase in frequency for the polyaniline - barium ferrite having[aniline]/[barium ferrite] ratio of 1:2(PBF12).

PEDOT-DBSA, the SE of the composite increases with the ferrite content exhibiting excellent frequency stability in the measured frequency range. PEDOT with higher ratio of [EDOT]/[Barium ferrite] of 1:2 (PEDOT-BaF12) has higher SE_A of 22.4 dB with nominal SE_R of 2dB as compared to SE_A value of 8dB and comparable reflection SE_R of 6dB for the PEDOT-DBSA. This shows that incorporation of the ferrite particles in the copolymer matrix leads to the improvement in the microwave absorption properties. The dependence of SE on complex permittivity and permeability can be expressed as [90]

$$SE_A(dB) = 20 \frac{d}{\delta} \log e = 20 d \sqrt{\frac{\mu_r \omega \sigma_{AC}}{2}} \cdot \log e$$
 (52)

$$SE_R(dB) = 10\log\left(\frac{\sigma_{AC}}{16\omega\mu_r\varepsilon_0}\right)$$
 (53)

where, d is the thickness of the shield, μ_r is the magnetic permeability, δ is the skin depth, $\sigma_{AC} = \omega \varepsilon_0 \varepsilon''$ is the frequency dependent conductivity, ε'' is imaginary part of permittivity (dielectric loss factor), ω is the angular frequency ($\omega = 2\pi f$) and ε_0 is the permittivity of the free space. From equations 52 & 53, it is observed that with the increase in frequency, the SE_A values increases while the contribution of the reflection decreases. Dependence of SE_A and SE_R on conductivity and permeability revel that the material having higher conductivity and magnetic permeability can achieve better absorption properties.



Fig. 26. Dependence of shielding effectiveness (SE_A & SE_R) as a function of frequency for PEDOT-DBSA, PEDOT-BaF11 and PEDOT-BaF12.

5.6 Dielectric properties of the conducting ferromagnetic nanocomposite

The electromagnetic absorption behaviour of a material depends on the dielectric properties represented by complex permittivity (ε' and ε'') and permeability (μ). The real part (ε') is mainly associated with the amount of polarization occurring in the material and the imaginary part (ε) is related to the dissipation of energy. The dielectric performance of the material depends on ionic, electronic, orientational and space charge polarization [93]. The contribution to the space charge polarization appears due to the heterogeneity of the material. As polyaniline is nonmagnetic, only complex permittivity (ɛ' and ɛ") contributes to the microwave absorption properties. The complex permittivity shown here has been obtained through scattering parameters S₁₁ and S₂₁ using Nicolson and Ross Technique [94, 95]. The real part of complex permittivity (ϵ) and imaginary part of complex permittivity (ϵ) vs. frequency are shown in figure 27. The real part of complex permittivity (ϵ) of polyaniline doped with DBSA is a function of dopant concentration and decreases with increase of DBSA concentration while the imaginary part of complex permittivity (ε") increases with increase of dopant concentration. The real part of complex permittivity (ϵ) and imaginary part of complex permittivity (ε) depend on the polarizability of the material, which in turn depend on the dipole density and their orientation. In case of polyaniline, there are two types of charged species, one polaron/bipolaron system which is mobile and free to move along the chain, the others are bound charges (dipoles) which have only restricted mobility and account for strong polarization in the system. When the frequency of the applied field is increased, the dipoles present in the system cannot reorient themselves fast enough to respond to applied electric field and as a result, dielectric constant decreases.

With the increase in the dopant concentration, the number of mobile charges increases which results in the higher dielectric loss ($\epsilon^{"}$) while the values of real part decreases. The polyaniline synthesized with monomer to dopant concentration of 3:1 (PD31) has dielectric constant (ϵ^{r} = 22.5 to 19.1) with dielectric loss ($\epsilon^{"}$ = 26.9 to 24.1) while the polyaniline with higher concentration ie molar ratio of monomer to dopant of 1:4(PD14) has dielectric constant (ϵ^{r} = 7.6 to 5.8) with imaginary permittivity ($\epsilon^{"}$ = 51.9 to 34.9).



Fig. 27. (a) Dielectric constant (ε) and (b) dielectric loss (ε ") of polyaniline having [aniline/DBSA] ratio of 3:1(PD31), 2:1(PD21), 1:1(PD11), 1:2(PD12) and 1:4 (PD14)

In case of polyaniline composite with barium ferrite, the real part (ϵ) has been found to be decreasing with the increase in frequency (Figure 28). The presence of insulating barium ferrite in the conducting matrix results in the formation of more interface and heterogeneous system due to which some space charge accumulates at the interface which contributes towards the higher microwave absorption in the composites. The contribution to the orientational polarization comes due to the presence of bound charges (dipoles). Firstly, in polyaniline, strong polarization occurs due to the presence of polaron/bipolaron and other bound charges which leads to high value of $\epsilon' \& \epsilon''$. With the increase in frequency, the dipoles present in the system cannot reorient themselves along with the applied electric field therefore, dielectric constant decreases.

Secondly, for the magnetic nanoparticles effective anisotropy, which includes magneto crystalline anisotropy and shape anisotropy, rotation of domain may become more difficult. Furthermore, the particle size of barium ferrite is in the range of nanometer. The surface area, number of dangling bond atoms and unsaturated coordination on the surface are all enhanced. These variations lead to the interface polarization and multiple scattering which are useful for the absorption of large number of microwaves [96, 97]. In polyaniline composites, both the phenomenon happen together resulting in high SE_A value. The polyaniline composite having higher ratio of 1:3 monomer to ferrite (PBF13) has lower dielectric constant (ϵ '=17) but higher dielectric loss (ϵ ''=34) and magnetic permeability (μ '=2.2) which corresponds to enhanced value of shielding effectiveness due to absorption.

In case of PEDOT, both, real and imaginary part of the permittivity remains constant in the measured frequency range (figure 29a & 29b) while in case of PEDOT-barium ferrite nanocomposites the incorporation of insulating barium ferrite in the conducting matrix shows higher values of ϵ' and ϵ'' as compared to PEDOT-DBSA and decreases with the



Fig. 28. Variation of (a) real and (b) imaginary part of permittivity with frequency. Figures c & d show the variation of real and imaginary part of magnetic permeability with frequency for the samples having [aniline/Barium ferrite] ratio of 2:1(PBF21), 1:1(PBF11), 1:2(PBF12) and 1:3(PBF13)



Fig. 29. Behavior of (a) real and (b) imaginary part of complex permittivity PEDOT-BaF composites as a function of frequency.

frequency. The higher values of ε' and ε'' arise due to the difference in the relative dielectric constant of barium ferrite and the PEDOT which results in the accumulation of more space charge and strong orientational polarization that consequently leads to the improved values of microwave absorption.

The variation in the real (μ) and imaginary (μ ") part of permeability with frequency for the PEDOT-BaF composites with different [EDOT]/[Barium Ferrite] ratios is shown in Figure 30 Real part of the permeability remains constant with a little fluctuation in the measured frequency range whereas the magnetic loss part slightly decreases with the frequency. Higher values of μ " have been observed for PEDOT-BaF12 as compared to PEDOT-BaF11 which confirms the existence of greater magnetic losses in PEDOT-BaF12 nanocomposite. The magnetic loss expressed by the imaginary part of complex permeability, mainly occur because of magnetic hysteresis and domain-wall displacement in the material.



Fig. 30. Variation of real and imaginary part of magnetic permeability of PEDOT-barium ferrite composite having [EDOT]/[Barium ferrite] ratio of 1:1(PEDOT-BaF11) and 1:2 (PEDOT-BaF12) s as a function of frequency

The permeability for the hexagonal ferrites having the c-axis as the preferred direction of magnetization is defined as [98]

$$\frac{(\mu-1)}{4\pi} = \left(\frac{2}{3}\right) \frac{M_s}{H_A} \tag{54}$$

where, M_s is the saturation magnetization and H_A is the anisotropy field. As the frequency increases, μ remains equal to its static (dc) value up to a critical frequency and then decreases with the further increase in frequency. Whereas, the imaginary part of permeability (μ ") starts increasing near the critical frequency and has a maxima at the resonance frequency which demonstrates the maximum power loss. The larger the static value of μ , the lower is the frequency at which this decrease occurs as given by Snoek's law [99]. The frequency of this precession depends on how strongly the magnetization is bound to the easy axis. The stronger the coupling, higher is the natural frequency of precession. The strength of this coupling depends on the value of the magneto-crystalline anisotropy K or the anisotropy field H_A , which is proportional to M_s [98]. In barium ferrite, due to the large anisotropy field, the coupling of the magnetic dipole is strong. When the frequency of the applied field increases, the magnetic dipole try to rotate with the frequency but at higher frequency due to strong anisotropy, the induced magnetization (B) lags behind the applied field (H) which results in magnetic losses. The larger is the anisotropy, higher is the difference in B and H and more are the magnetic losses occurring in the material [100]. In magnetic nanoparticles, the rotation of domains becomes difficult due to the effective anisotropy (magneto-crystalline anisotropy and shape anisotropy). The effective anisotropy coefficient can be enhanced significantly with decreasing particle size due to the surface effect and microstructure defects [101, 102]. Therefore, the increase in barium ferrite content in the polymer matrix leads to higher magnetic loss which in turn enhances absorption of the microwaves. The dielectric and magnetic loss in the whole frequency range provides the balanced property of EM matching in the composite suggesting that the enhanced microwave absorption properties unambiguously results from the cooperative effect of PEDOT shell and ferrite cores.

6. Improvement in electromagnetic shielding properties of conducting ferromagnetic nanocomposites via dielectric filler TiO₂

Polymeric materials with high dielectric constants are highly desirable for use in actuators, artificial muscles and charge-storage devices [103,104]. To raise the dielectric constant of polymers, high-dielectric constant ceramic powders such as BaTiO₃ and PbTiO₃ have been added to the polymers to form nanocomposites [105-110]. The electrical properties of polyaniline could be modified by the addition of inorganic fillers [111-116]. Nanoscale fillers are the most attractive due to the intriguing properties arising from the nanosize and large surface area. The insertion of nanoscale fillers may improve the electrical and dielectric properties of host materials. A high-dielectric constant up to 3700 for polyaniline-TiO₂ nanocomposite materials has been reported by Dey et al. [115]. However, high-dielectric constants are usually accompanied with high-dielectric losses. Xu et al. [117] noticed that the electrical conductivity of a polyaniline-TiO₂ nanocomposite with a low TiO₂ content is much higher than of polyaniline. Su et al. [118] reported that the polyaniline-TiO₂ nanocomposite has suitable conductivity (1-10 S/cm) and increases after thermal treatment at 80°C for 1h. Due to moderate conductivity and high dielectric losses, these polymer composites found its application as microwave absorber.



Fig. 31. Schematic representation of the interaction of microwave with PBT nanocomposites incorporating barium ferrite and TiO_2 nanoparticles

In this section, the effect of TiO_2 nanoparticles on the dielectric and microwave absorption properties of the polyaniline-barium ferrite composite has been discussed. The incorporation of dielectric filler and magnetic filler in the polyaniline matrix enhances the absorption of the microwave to a large extent. The interaction of microwave with TiO_2 incorporated polyaniline –Barium ferrite (PBT) nanocomposites is shown in figure 31.

6.1 Incorporation of TiO₂ nanoparticles in polyaniline-barium ferrite nanocomposite

The nano-sized barium ferrites along with TiO_2 nanoparticles have been homogenized in 0.3M aqueous solution of dodecyl benzene sulfonic acid (DBSA) to form a whitish brown emulsion solution. Appropriate amount of aniline (0.1M) has been added to the above solution and again homogenized for 2-3 hours to form micelles of aniline with barium ferrite and TiO_2 . The micelles so formed have been polymerized at -2°C by emulsion polymerization using (NH₄)₂S₂O₈ (0.1 M) which act as oxidant (figure 32). The product so obtained has been demulsified by treating it with equal amount of isopropyl alcohol. The precipitates so obtained have been filtered out, washed with alcohol and dried at 60-65°C in vacuum oven.



Fig. 32. Schematic representation of polymerization of micellar solution of DBSA containing the barium ferrite and TiO_2 nanoparticles using APS as oxidant

6.2 X-ray diffraction studies

Figure 33 shows the X-ray diffraction patterns of TiO₂, barium ferrite and Polyanilinebarium ferrite-TiO₂ (PBT) nanocomposites. The main peaks for TiO₂ have been observed at 20 value 25.283° (d=3.520 Å), 37.784° (d=2.379 Å), 38.530° (d=2.335 Å), 48.032° (d=1.893 Å), 53.874° (d=1.700 Å), 55.025° (d=1.667 Å) and 62.660° (d=1.481 Å) corresponding to (101), (004), (112), (200), (105), (211) and (204) reflections, respectively (curve a). For barium ferrite, main peaks have been observed at 20 value of 30.294° (d=2.9480), 32.141° (d=2.7827), 34.083° (d=2.6284), 37.046° (d=2.4247), 40.254° (d=2.2386), 42.391° (d=2.1305), 55.018° (d=1.6677), 56.477° (d=1.6280) and 63.054° (d=1.4731) corresponding to the (110), (107), (114), (203), (205), (206), (217), (2 01) and (22 0) reflections, respectively (curve f).

The peaks of barium ferrite have been observed in all the compositions of polyaniline composites with TiO_2 and barium ferrite which indicate the presence of ferrite particles in the polymer matrix. The increase in the intensity of the peaks demonstrates the increase in the ratio of barium ferrite. The presence of peaks of TiO_2 and barium ferrite shows the formation of composite having separate phases of both the compounds dispersed in the polymer matrix.



Fig. 33. (a) X-ray diffraction patterns of (a) TiO₂, (b) polyaniline-TiO₂ (PT11), polyaniline-Barium ferrite-TiO₂ composite with [Barium ferrite]/ [TiO2] ratio of (c) 2:1(PBT21), (d)1:1(PBT11), (e) 1:2 (PBT12) and (f) barium ferrite.

6.3 TEM & HRTEM analysis

Figure 34 illustrates the TEM & HRTEM images of the TiO₂, polyaniline-TiO₂ (PT11) and polyaniline-barium ferrite-TiO₂ composite. Figure 34a shows the TiO₂ particles of size 60-80nm. When these nano particles of TiO₂ & barium ferrite have been polymerized along with aniline, they form a core shell type of morphology. From the figure 34c, it has also been observed that an array of nanoparticles is formed during the in-situ emulsion polymerization process which directly indicates that the particles are connected by the polymer matrix. The presence of conducting shell encapsulating the magnetic and dielectric nanoparticles is helpful in enhancing the absorption of the electromagnetic wave in the nanocomposite. The presence of other elements in the polymer composite has been confirmed by energy dispersive X-ray spectroscopy (EDS) (figure 34h & 34i)

6.4 UV-visible analysis

Figure 35 shows the UV-visible spectra of polyaniline doped with DBSA (PD13), polyaniline-TiO₂ (PT11), polyaniline-Barium ferrite-TiO₂ composite with [Barium ferrite]/ [TiO2] ratio of 2:1(PBT21), 1:1(PBT11),1:2 (PBT12) in chloroform medium. Polyaniline doped with DBSA in CHCl₃ medium exhibit three characteristic bands; at 352nm due to π - π * transition, at 433nm and 737 nm due to the charged cationic species, known as polaron. However, in the case of PBT12 composite, the main transitions have been observed at 374 nm and 711 nm and the peak at 430 nm has been suppressed due to the presence of barium ferrite and TiO₂. The shift in the polaronic band towards the lower wavelength is attributed to the presence of barium ferrite and TiO₂ nanoparticles that interact with the -NH group of polyaniline ring which contributes to the decrease in conductivity of the PBT12 composite as compared to the polyaniline doped with DBSA. From the UV-Vis spectra, the degree of doping is estimated from the ratio of absorption at polaronic transition to π - π * transition (A_{polaronic}/A_{π - π *) as shown in table 2.}



Fig. 34. Transmission electron micrograph of (a) TiO_2 , (b) Barium ferrite and TiO_2 in ratio of 2:1 and (c) polyaniline-Barium ferrite- TiO_2 composite with [Barium ferrite]/ [TiO2] ratio of 1:2(PBT12) nanocomposites showing the formation of array of nanoparticles via conducting matrix of polyaniline. (d) High-resolution TEM images of Polyaniline- TiO_2 (PT11), (e) PBT21 and (f & g) PBT12. Fringes indicate the presence of crystalline (f) barium ferrite and (g) TiO_2 particles, while outer shell shows the polymer matrix of PBT12 nanocomposite. The inset to figure (e) demonstrates the electron diffraction pattern of PBT12 having ring of crystalline barium ferrite and TiO_2 . Energy dispersive X-ray spectroscopy (EDS) of (h) PT11 and (i) PBT12 showing the approximate percentage of the element present in the nanocomposite



Fig. 35. UV/Visible spectra of PBT12, PBT11, PBT21, PT11, PBF12 nanocomposites and DBSA doped polyaniline (PD13)

Sample name	Conductivity at 300K (S/cm)	UV-visible bands		Degree of doping	
		Polaronic bands	π-π*	$(A_{polaronic}/A_{\pi-\pi^*})$	
PD13	2.2	737, 430	353	2.24	
PT11	0.13	730	374	0.24	
PBF12	0.08	729	384	0.11	
PBT21	0.4	713	378	0.68	
PBT11	0.27	716	362	1.25	
PBT12	0.3	711	374	0.75	

Table 2. Room temperature conductivity, UV-Vis. bands and the degree of doping for different samples.

6.5 Conductivity measurement

The temperature dependent dc conductivity (σ_{dc}) of the PT11 and PBT composites having different weight ratio of barium ferrite has been measured in the temperature range of 30-300K. The variation of $\log \sigma_{dc}$ as function of T^{-1/4} has been plotted in figure 36 whereas, inset shows the $\log \sigma_{dc}$ vs. 1000/T plot. From the inset, it is evident that the dc conductivity tends to saturate in the low temperature region. In order to explain the conduction mechanism,

Mott's variable range hopping (VRH) model has been used. In hopping conduction process each state can have only one charge carrier for each spin direction. In the case of strong localization, the charge carrier will hop to a nearest neighboring state and the hopping conductivity will be proportional to Boltzmann's factor $\exp(-W/K_BT)$, where, W is the difference of energy between two states and is called hopping energy or activation energy required for a charge carrier to hop from one site to another site. However, when charge carriers are not strongly localized, a charge carrier can jump to the sites for which the activation energy is small and can reside further away and then the transport occurs by variable range hopping. According to Mott's VRH model [43], the conductivity can be expressed as

$$\sigma(T) = \sigma_O \exp\left[-\left(\frac{T_O}{T}\right)^{\gamma}\right]$$
(55)

where, σ_o and T_o are constants and exponent γ is the dimensionality factor having values 1/2, 1/3, 1/4 for 1 dimension, 2 dimensions and 3 dimension conduction mechanism. In order to calculate the exponent γ , log σ_{dc} vs. T^{-1/4} is plotted which yields a linear behavior for the temperature range of 70-300K. To satisfy the Mott's equation, activation energy [119-121]

$$E_A = \left\{ -\partial \ln \sigma / \partial (1 / K_B T) \right\}$$
(56)

of the samples has been calculated from the slope of $\log\sigma_{dc}$ vs. 1000/T plot. The hopping conduction has been confirmed from the $\log\sigma_{dc}$ vs. 1000/T curve which shows that the activation energy of the polymer composites changes with temperature. For 3-D conduction mechanism, the values of Mott characteristic temperature (T_o) and σ_o (conductivity at T= ∞) are given by

$$T_O = 16\alpha^3 / \left[k_B N(E_F) \right] \tag{57}$$

$$\sigma_O = e^2 R^2 \nu_{ph} N(E_F) \tag{58}$$

$$R = \left[9 / \left\{8\pi\alpha K_B T N \left(E_F\right)\right\}\right]^{1/4}$$
(59)

where, R is the average hopping distance, α^{-1} is the localization length, N(E_F) is the density of states at the Fermi level, and ν_{ph} is the phonon frequency (~10¹³ Hz).). The average hopping energy W can be estimated by knowing the average hopping distance R and the density of states at the Fermi level N(E_F) by the following relation

$$W = \frac{3}{4\pi R3N(E_F)}$$
(60)

Using the above equations, various Mott's parameters can be calculated. The conductivity data fits for the 3D- VRH model having $\gamma = 1/4$, the linearity factor of 0.9997 for PT11, 0.9991 for PBT11 and 0.998 for PBT12 nanocomposite has been calculated from 300-70K. It is observed from figure 36 that the variation of conductivity deviates from the linear



Fig. 36. The variation of dc conductivity (σ_{dc}) as a function temperature in the range 30-300 K for PBT11, PBT12 and PT11 nanocomposites

behavior towards the lower temperature (< 70 K) which reveals that the 3D-VRH is applicable for the temperature higher than 70K. Thus, it has been concluded that 3D-VRH model is suitable for explaining the conduction mechanism wherein the charge transport occurs by phonon aided hopping or by thermally stimulated jumps between the localized sites [122, 123]. The new states are generated between the valence and conduction bands by the doping and are responsible for conduction and lead to the variation in activation energy. The overlapping of π -delocalized wave orbital of aniline ring with the d-orbital of metal ion in polymer composite forms the charge transfer complex site which act as the localized states from where the hoping of charge carrier take places.

Below 70 K, it has been observed that conductivity data deviates from the linear behavior because in low temperature region charge conduction is mainly dominated by the thermally stimulated tunneling through the localized sites as reported earlier for the other conjugated polymers. Conductivity at 300K (table 2) for polyaniline DBSA and polyaniline composites demonstrates the effect of nanoparticles on conductivity. It is observed that with the addition of nanoparticles of BaFe₁₂O₁₉ (σ ~10⁻⁸S/cm) and TiO₂ (σ ~10⁻¹¹S/cm) in the polymer matrix, the conductivity of the polyaniline doped with DBSA decreases from 2.2 S/cm to 0.3 S/cm for PBT12 composite. The expected decrease in conductivity is due to the incorporation of insulating nanoparticles in the polymer matrix which hinder the conduction path in the polyaniline.

6.6 Magnetic studies

VSM studies have revealed the saturation magnetization value (Ms) of barium ferrite particles to be 52emu/g (figure 37) whereas, the incorporation of ferrite particles in the polymer matrix leads to saturation magnetization (Ms) value of 29emu/g for PBT12 sample. From the hysteresis loop of barium ferrite and polyaniline nanocomposites, it has been observed that the material possesses high retentivity (Mr) and coercive force (Hc).



Fig. 37. Magnetization curves of barium ferrite (BaF) and polymer nanocomposites PBT21, PBT11 and PBT12, showing the increase in saturation magnetization with the barium ferrite content

The observed hysteresis loop shows little variation from the regular magnetization curve of barium ferrite which may be attributed to annealing conditions and also to the increase in the iron concentration [124]. This type of behavior is observed in ferrites having high Curie temperature and to the slow cooling of the sample which causes slight oxidation of the sample. It is also found that by changing the ratio of barium ferrite in the polyaniline nanocomposites, the saturation magnetization (Ms) value increases with increase of ferrite.

6.7 Shielding measurements

Figure 38 shows the variation of the SE with frequency in the 12.4-18 GHz range. As seen in the figure, PBF12 shows the SE_A value of 19dB while for PT11 nanocomposite, the SE_A value of 22dB is observed. With the addition of barium ferrite nanoparticles in the ratio 2:1 and 1:1, increase in microwave absorption is nominal (~3dB) but, when double amount of barium ferrite is taken as compared to TiO_2 (sample PBT12), substantial enhancement in the absorption of electromagnetic radiation is observed. The maximum shielding effectiveness of 58dB has been achieved for the sample PBT12 having the polymer: TiO_2 :ferrite ratio of 1:1:2. It is observed that the shielding effectiveness increases with the increase in ferrite concentration and with the increase of frequency. The increase in the absorption part is mainly attributed to be due to the presence of a high dielectric constant material and a magnetic material which increase more scattering which in turn results in more attenuation of the electromagnetic radiations (Figure 38).



Fig. 38. Dependence of shielding effectiveness (SE_A & SE_R) on frequency showing the effect of barium ferrite concentration on the SE_A value of the nanocomposites

Figure 39a (inset) shows the variation of σ_{AC} with the frequency for the sample PBT11, calculated from the dielectric measurements ($\sigma_{ac} = \omega \varepsilon_0 \varepsilon''$).To correlate σ_{AC} with the shielding parameters of the material, SE_R is plotted against log σ_{AC} (figure 39a). Higher value of conductivity is required for high shielding effectiveness due to reflection. For the absorption part, the skin depth of the samples has been calculated using the relation, $\delta = \sqrt{2 / \omega \mu \sigma_{AC}}$ and its variation with frequency is shown in figure 39b (inset). It has been observed that the skin depth decreases with frequency which demonstrates that mainly surface conduction exists at the higher frequencies. The dependence of skin depth on the conductivity and magnetic permeability reveal that, for highly conducting and magnetic material, the skin depth is very small. The dependence of SE_A on (σ_{AC}) ^{1/2} is shown in figure 39b.

6.8 Dielectric & permeability studies

The main characteristic feature of TiO_2 is that it has high dielectric constant with dominant dipolar polarization and the associated relaxation phenomenon constitutes the loss mechanism [93]. With the addition of barium ferrite and TiO_2 in polyaniline matrix, significant increase in the imaginary part of complex permittivity has been observed. The higher values of the dielectric loss is attributed to the more interfacial polarization due to the presence of insulating barium ferrite particles and high dielectric constant (TiO₂) particles which consequently leads to more shielding effectiveness due to absorption.

Figure 40 (c & d) shows the variation of real part and imaginary part of magnetic permeability with frequency. The magnetic permeability of all the samples decreases with the increase in frequency whereas, higher magnetic loss has been observed for higher percentage of barium ferrite (PBT12) in the polymer matrix. The magnetic loss is caused by the time lag of magnetization vector (M) behind the magnetic field vector. The change in magnetization vector is generally brought about by the rotation of magnetization and the domain wall displacement. These motions lag behind the change of the magnetic field and



Fig. 39. (a) Variation of SE_R as a function of log σ_{AC} while the inset shows the variation of σ_{AC} with the increase in frequency and (b) variation of SE_A as function of $(\sigma_{AC})^{1/2}$ while the inset shows the change in skin depth (δ) with the increase in frequency for the sample PBT12

contribute to the magnetic loss (μ ") [125]. The rotation of domain of magnetic nanoparticles might become difficult due to the effective anisotropy (magneto-crystalline anisotropy and shape anisotropy). The surface area, number of atoms with dangling bonds and unsaturated coordination on the surface of polymer matrix are all enhanced [126-128]. These variations lead to the interface polarization and multiple scattering which is useful for the absorption of large number of microwaves.



Fig. 40. Behavior of (a) real and (b) imaginary part of permittivity. Figures (c) & (d) show the variation of real and imaginary part of magnetic permeability with the change in frequency for the samples PBT12 (\blacktriangle), PBT11 (\bullet), PBT21 (\blacksquare), PBF12 (\blacktriangleleft) and PT11 (\bigtriangledown)

7. Conclusion

The enhancement in the microwave shielding and absorption properties of the polyaniline nanocomposite has been achieved by the incorporation of dielectric filler (TiO₂) along with the magnetic filler (barium ferrite) in the polyaniline matrix. TEM and HRTEM images demonstrate that in the polyaniline-barium ferrite-TiO₂ (PBT) nanocomposites, barium ferrite and TiO₂ nanoparticles form the array of nanoparticles connected via conducting polyaniline system. These conducting paths of polyaniline between the magnetic and dielectric nanoparticles increase the absorption of the electromagnetic wave to a large extent. The high shielding effectiveness of 58dB due to absorption has been achieved for these composites. The contribution to the absorption value comes mainly due the magnetic losses (μ ") in barium ferrite and dielectric losses (ϵ ") in TiO₂ and polyaniline. The dependence of SE_A on magnetic permeability and conductivity demonstrates that better absorption value can be obtained for materials with higher conductivity and magnetization. Therefore, from the present studies, it can be concluded that the incorporation of magnetic

and dielectric fillers in the polymer matrix lead to better absorbing material which make them futuristic radar absorbing material.

In spite of these interesting developments, a lot remains to be done with regard to both fundamental understanding and the much needed improvement of the method of the designing of electromagnetic shielding materials to operate at higher frequencies for their application.

8. References

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Electrospinning Fabrication and Characterization of Water Soluble Polymer/Montmorillonite/Silver Nanocomposite Nanofibers out of Aqueous Solution

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1. Introduction

Polymer nanocomposites are a class of materials that have properties that offer significant commercial potential. It was commonly defined as the combination of a polymer matrix resin and inclusions that have at least one dimension (i.e. length, width, or thickness) in the nanometer size range. There are many types of nanocomposites that have received significant research and development including polymer/inorganic particle, polymer/polymer, metal/ceramic, and inorganic based nanocomposites. These polymer hybrid nanocomposites have attracted great interest due to inorganic materials filled polymer composites often exhibit remarkable improvement in material properties with only a low percentage of inorganic materials. High degrees of stiffness, strength, conductivity and thermal resistance, etc. are realized with far less high density inorganic material, they are much lighter compared to conventional polymer composites. Many novel nanocomposites with improved performance properties, which may have large potential applications in the fields such as optics, electrical devices, and photoconductors were reported (Fleming et al., 2001; Luna-Xavier et al., 2001; Tiarks et al., 2001).

The synthesis of polymer nanocomposites is normally carried out by the following methods. One is based on in-situ polymerization of monomers inside the galleries of the inorganic host (Messersmith & Giannelis, 1993). The other approach is based on melt intercalation of polymers and it involves annealing a mixture of the polymer and the inorganic host, statically or under shear, above the T_g of the polymer (Usuki et al., 1997; Vaia et al., 1995). The solventless melt intercalation is an environmentally friendly technique and is adoptable to existing processing like roll milling, extrusion and molding. The materials made via these two processes have been summarized. Other unique methods for blending polymers directly with inorganic materials have employed microwaves, latex-colloid interaction, solvent evaporation, spray drying, spraying a polymer solution through a small orifice and Shirasu Porous Glass (SPG) membrane emulsification technique (Berkland et al., 2001; Fischer et al., 1999; Mu & Feng, 2001; Oriakhi & Lerner, 1995; Rosca et al., 2004).

The other techniques for preparing polymer nanocomposites is electrospinning process that has attracted great interest among academic and industrial scientists because it is very simple, low cost, and effective technology to produce polymer nanocomposite nanofibers which has been exhibit outstanding properties such as a high specific surface area and high porosity. These nanofibers can be used for a wide variety of applications such as separation filters, wound dressing materials, tissue scaffold, sensors, protective clothing, catalysis reaction, etc. (Choi et al., 2004; Han et al., 2006; Huang et al., 2003; Li & Xia, 2004; Reneker & Chun, 1996; Wang et al., 2002; Wu et al., 2005; Zussmas et al., 2003). Biomedical field is one of the important application areas. By utilizing electrospinning technique this field can be enriched widely. Different group have reviewed recently the patents and worked on electrospun biomedical nanostructures like tissue engineering, drug delivery and scaffold engineering (Min et al., 2004; Sangamesh et al., 2008; Vasita & Katti, 2006). In a typical electrospinning process, a high voltage is applied to a polymer fluid such that charges are induced within the fluid. When charges within the fluid reached a critical amount, a fluid jet will erupt from the droplet at the tip of the needle resulting in the formation of a Taylor cone. The electrospinning jet will travel towards the region of lower potential, which in most cases, is a grounded collector. There are many parameters that will influence the morphology of the resultant electrospun fibers, from beaded fibers to fibers with pores on its surface. The parameters affecting electrospinning and the fibers mat are broadly classified into polymer solution parameters, processing conditions which include the applied voltage, temperature and effect of collector, and ambient conditions. With the understanding of these parameters, it is possible to create nanofiber with different morphology by varying parameters.

Here, we have been fabricated several electrospun nanocomposite nanofibers in aqueous solutions with poly(vinyl alcohol) (PVA), chitosan oligosaccharide (COS), and pullulan (PULL) as polymer matrixs, and montmorillonite (MMT) and silver(Ag) nanoparticles as inorganic materials. The effectiveness of these nanocomposite nanofibers are demonstrated with a field emission-type scanning electron microscope (FE-SEM), a transmission electron microscopy (TEM), a reflection type X-ray diffraction (XRD), Fourier transform spectroscopy (FT-IR), Thermogravimetric analysis (TGA), differential scanning calorimeters (DSC) and the anti-bacterial performance was also discussed.

2. Background

MMT is one of the most useful inorganic material for nanocomposite, it has attracted great interest due to MMT filled polymer nanocomposites often exhibit remarkable improvement in material properties such as mechanical, thermal, flame-retardant, and barrier properties with only a low percentage of MMT fillers added. These property improvements are attributed to the nanometric thickness and high aspect ratio of the individual clay platelets, as well as to the nanocomposite morphology with the platelets being exfoliated and well-dispersed (Gates et al., 2000; Svensson et al., 2010).

Ag nanoparticles are widely used as a photosensitive components, catalysts and chemical analysis. Additionally, due to its comparatively high safety, many researchers have successfully developed antibacterial and disinfectant agents with silver composite using various polymers. Microorganisms with resistance to the antimicrobial activity of Ag are exceedingly rare. Such silver has a size of nano-level, the total surface area of the silver become larger in identity volume and antibacterial efficiency is increased (Glaus et al., 2002; Rujitanaroj et al., 2008).



Fig. 1. Schematic representation of polymer/MMT nanocomposites



Fig. 2. SEM photograph of Ag nanoparticles

PVA is a semi-crystalline hydrophilic polymer with good chemical and thermal stability. Also, it has highly biocompatible and non-toxic. It can be processed easily and has high water permeability. These properties have led to the use of PVA in a wide range of applications in medical, cosmetic, food, pharmaceutical, and packaging industries. Especially, PVA has been used in fiber and film products for many years. Ultrafine PVA fibers, which may have different potential applications than microfibers, cannot be produced by conventional spinning techniques (Yeum et al., 2004).

Chitosan, the second most abundant polysaccharide in nature after cellulose, is an N-deacetylated derivative of chitin. It is generally regarded as non-toxic, biocompatible and biodegradable. It has many unique functional properties for different applications like high molecular weight, high viscosity, high crystallinity and capacity to hydrogen bond intermolecularly. However, the rigid D-glucosamine structure and high crystallinity in chitosan usually lead to poor solubility of chitosan in common organic solvents as well as in water, such as at physiological pH values (7.2–7.4), restricting its uses, especially in human body. However, partially depolymerized chitosan products, i.e., low molecular weight chitosan (COS), could overcome these limitations and hence find much wider applications in diversified fields (Kumar et al., 2004).



Fig. 3. Schematic representation of interaction(a) PVA/MMT/Ag, (b) PULL/MMT and (c) PVA/COS/MMT nanocomposite nanofibers

PULL is an extracellular microbial polysaccharide produced by the fungus-like yeast, Aureobasidium Pullulans (Yuen, 1974). It is a polysaccharide polymer consisting of maltotriose units, also known as α -1,4-; α -1,6-glucan. Three glucose units in maltotriose are connected by an α -1,4 glycosidic bond, whereas consecutive maltotriose units are connected to each other by an α -1,6 glycosidic bond. The regular alternation of (1 \rightarrow 4) and (1 \rightarrow 6) bonds results in two distinctive properties of structural flexibility and enhanced solubility (Leathers, 1993). The unique linkage pattern also endows PULL with distinctive physical traits along with adhesive properties and its capacity to form fibers, compression moldings, and strong, oxygen impermeable films. Due to its excellent properties, PULL is used as a low-calorie ingredient in foods, gelling agent, coating and packaging material for food and drugs, binder for fertilizers and as an oxidation-prevention agent for tablets. Other applications include contact lenses manufacturing, biodegradable foil, plywood, water solubility enhancer and for enhanced oil recovery (Israilides, 1998; Leathers, 2003; Schuster, 1993). It is water soluble, insoluble in organic solvents and non-hygroscopic in nature. Its aqueous solutions are stable and show a relatively low viscosity as compared to other polysaccharides. It decomposes at 250–280 °C. It is moldable and spinnable, being a good adhesive and binder. It is also non-toxic, edible, and biodegradable.

3. Experimental

3.1 Materials

PVA with P_n (number-average degree of polymerization) = 1700 [fully hydrolyzed, degree of saponification (DS)=99.9%] was obtained from DC Chemical Co., Seoul, Korea. COS (Average molecular weight above 10,000; 100% water soluble) was purchased from Kittolife Co., Kyongki-do, Korea and used without further purification. PULL was a food grade preparation (PF-20 grade) from Hayashibara Biochemical Laboratories Inc. (Okayama, Japan). MMT was purchased from Kunimine Industries Co. Ltd., Japan and aqueous Ag nanoparticle dispersion (AGS-WP001, 10,000 ppm) with diameters ca.15-30 nm was got from Miji Tech., Korea. Doubly distilled water was used as a solvent to prepare all solutions.

3.2 Electrospinning nanocomposite nanofibers



Fig. 4. Schematic representation of the electrospinning process and SEM image of PVA nanofibers at different conditions

During electrospinning, a high voltage power (CHUNGPA EMT Co., Korea) was applied to the polymer/inorganic material blend solution contained in a syringe via an alligator clip attached to the syringe needle. The applied voltage was adjusted at 15 kV. The solution was delivered to the blunt needle tip via syringe pump to control the solution flow rate. Fibers were collected on an electrically grounded aluminum foil placed at 15 cm vertical distance to the needle tip (Tip-Collector Distance, TCD). The above spinning conditions were found being the best condition to make PVA based nanofibers in our previous report (Ji et al., 2009; Karim et al., 2009; Lee et al., 2009a; Lee et al., 2009b; Park et al., 2009; Park et al., 2010).

Nanocomposite nanofiber		Total polymer	Blend ratios	Contents*	
		concentration		MMT	Ag
Two types inorganic material	PVA	7.5 wt.%	-	-	-
	PVA/MMT			5 wt.%	
	PVA/MMT/Ag			5 wt.%	5 wt.%
	PVA/COS	12.5 wt.%	6/4	-	
			8/2		
Two types			10/0		
polymer			6/4	5 wt.%	-
	PVA/COS/MMT		8/2		
			10/0		
		20 wt.%	-	1 wt.%	
Natural				3 wt.%	
polymer				5 wt.%	
				10 wt.%	

* based on total polymer concentration

Table 1. Experimental condition for the preparation of nanocomposite nanofibers

4. Results and discussion

4.1 PVA/MMT/Ag nanocomposite nanofibers 4.1.1 Morphology and structure property

Figure 5 demonstrates FE-SEM and TEM images of PVA, PVA/MMT and PVA/MMT/Ag nanofibers electrospun with 5 wt.% of MMT and 5 wt.% of Ag nanoparticles. MMT contents were important parameters which had effects on the morphology of electrospun PVA nanofibers. The diameter of nanofibers increases but fibers homogeneity decreases with MMT contents. In the TEM image, the size of the dark line is about 1–3nm in width and 100–200nm in length, indicating the good dispersion and exfoliation of MMT layers in the nanofibers. This clearly indicates the feasibility of electrospinning of the 2-D platelet structures and the potential to achieve proper alignment of these clays along the fiber axis, which is critical for nanocomposite fiber fabrication. The Ag nanoparticles distribution along

the fiber direction and on the fiber cross-section is detected by TEM. It is seen that the MMT and Ag nanoparticles are distributed uniformly in nanofibers.



Fig. 5. FE-SEM and TEM images of (a), (b) pure PVA, (c), (d) PVA/MMT, (e), (f) PVA/MMT/Ag nanocomposite nanofibers

The XRD pattern (Fig. 6) of PVA/MMT/Ag nanocomposite nanofibers show diffraction peaks at 2 θ of ca. 19.3° 38.2° and 44.6°, respectively [Fig. 6(c-e)]. The pure PVA nanofibers show a significant crystalline peak at about 19.3°, which is because of the occurrence of string inter- and intramolecular hydrogen bonding (Fig. 6a). In case of a clay-polymer composite, unexfoliated or intercalated MMT usually show a peak in the range 3~9° (2 θ) (Fig. 16). In exfoliated nanocomposites, generally single silicate layers (1-3 nm thick) are homogeneously dispersed in the polymer matrix, and XRD patterns with no distinct diffraction peak in the range of 3~9° (2 θ) could be observed (Fig. 6b) (Barber et al., 2005; Zhu et al., 2007). Except the diffraction peaks of PVA, all the other peaks are corresponding to the silver phase [Fig. 6 (c-e)]. The peaks of Ag are enlarged with increasing the content of Ag nanoparticles and crystallinity of PVA/MMT (2 θ =19.3°) is lower in comparison with Figure 6b. These peaks are corresponding to the 111 and 200 planes of the silver nanocrystals with

cubic symmetry. XRD results indicate that MMT and Ag particles are well dispersed in the PVA nanofibers and MMT is predominantly exfoliated. TEM images further confirm MMT (Fig. 5d) and Ag nanoparticles (Fig. 5f) in the PVA/MMT/Ag nanocomposite nanofibers.



Fig. 6. XRD data of PVA/MMT/Ag nanocomposite nanofibers prepared with different Ag contents of 0 wt.%, 1 wt.%, 3 wt.% and 5 wt.%



Fig. 7. Schematic representation of PVA/MMT/Ag nanocomposits

4.1.2 Thermal stability

Thermal stability of electrospun PVA, PVA/MMT and PVA/MMT/Ag nanofibers were measured using TGA in nitrogen atmosphere. Figure 8 shows TGA thermograms of different decomposition temperature with MMT and Ag contents. The most below curve of the TGA data (Fig. 8a) represent the pure PVA and the most upper curve (Fig. 8e) is for mass ratio of 5 wt.% of Ag nanoparticles i.e. the highest mass ratio of Ag contents is used in our work. Generally, when PVA is pyrolyzed in the absence of oxygen, it undergoes dehydration and depolymerization at temperature over 200 °C and 400 °C, respectively. The actual depolymerization temperature depends on the detail structure, molecular weight and conformation of the polymer. Figure 8(c, d) are displaying the middle masses ratio of Ag contents at the same trend of thermal stability like the Figure 8(a, e). Within up to 225 °C,
there is increased in thermal stability from the pure PVA nanofibers to PVA/MMT/Ag nanofibers. The higher thermal stability of high MMT and Ag content rate might be attributed to its higher chain compactness due to the interaction between the PVA, MMT and Ag nanoparticles.



Fig. 8. TGA data of pure PVA nanofibers and PVA/MMT/Ag nanocomposite nanofibers prepared with different Ag contents of 0 wt.%, 1 wt.%, 3 wt.% and 5 wt.%

4.1.3 Anti-bacterial efficacy

The preservation efficacy for the PVA/MMT/Ag nanofiber was tested to evaluate the antimicrobial property (Farrington, 1994). Samples were prepared by dispersing the nanofibers in a viscous aqueous solution containing 0.01 wt.% of neutralized polyacrylic



Fig. 9. Preservation performance of PVA/MMT/Ag nanocomposite nanofibers prepared with different Ag contents of 0 wt.%, 1 wt.%, 3 wt.% and 5 wt.%

acid (Carbopol 941, Noveon Inc.). A mixed culture of microorganisms, *Staphylococcus aureus* (ATCC6538), and *Escherichia coli* (ATCC25922) were obtained on tryptone soya broth after 24h incubation at 32 °C. Then, 20g of samples were inoculated with 0.2g of the microorganism suspensions to adjust the initial concentration of bacteria to 107 cfu/g. Then, the inoculant mixed homogeneously with the samples and was stored at 32 °C. The microbial counts were carried out using the pour plate count method.

As shown in Figure 9, the PVA/MMT/Ag nanofibers without Ag fail to have the antibacterial performance. The number of bacteria in the test samples remains constant for a long time. On the contrary, the incorporation of the PVA/MMT/Ag nanofibers into the test samples result in a remarkable decrease in the number of bacteria. The increase in the concentration of the Ag nanoparticles in nanofibers accelerates diminishing in bacteria. With only a small amount of Ag, almost all the initially inoculated bacteria could be sterilized within a week. This indicates that the PVA/MMT/Ag nanofibers have an anti-bacterial activity.

4.2 PVA/COS/MMT nanocomposite nanofibers 4.2.1 Morphology and structure property

Changing the polymer mass ratio of PVA/COS and the MMT content in the composite could alter the fiber diameter and morphology very effectively, as show in Figure 10. At the



Fig. 10. FE-SEM images of PVA/COS and PVA/COS/MMT nanocomposite nanofibers prepared with different polymer blend ratios (MMT 5wt.%)

operation voltage of 15kV and tip to collector distance of 15cm, a series of nanofibers was made at a fixed total solid content (12.5 wt.%) but various PVA/COS mass ratio (6/4, 8/2 and 10/0) and 5 wt.% MMT contents (based on the total solid content). It should be noted that, when the PVA/COS mass ratio in the blend solutions is higher than 6/4, the viscosity of the solution is too low to be electrospun.

Figures 10 shows dramatic morphological changes as the mass of COS and concentration of MMT. By carefully comparing the SEM images shown in Figure 10, we found that fiber diameter show opposite tendency by COS ratio. It is known that the diameter of fibers and the formation of beads are strongly influenced by the viscoelasticity of the solution (Fong et al., 1999). Uniform nanofibers with diameters of 200-400 nm were obtained and no any beads were observed for PVA/COS ratios of 6/4 and 8/2. It was also noticed that the fiber diameter of PVA/COS is ~200 nm at a PVA/COS mass ratio of 6/4, which is much smaller than the diameter of fibers obtained at a PVA/COS ratio of 8/2. If total polymer concentrations are lower than 12.5 wt.%, some small "beads" are presented in nanofibers were aggregated and the homogeneity of the nanofibers was decreased. It can be concluded that, from the above discussion, the PVA/COS mass ratio and MMT content in the blend solutions are two important parameters which have remarkable effects on the morphology of electrospun sub-micron fibers of PVA/COS/MMT blend.



Fig. 11. TEM images of PVA/COS/MMT nanocomposite nanofibers prepared with different MMT contents of (a) 0 wt.%, (b) 1 wt.%, (c) 3 wt.%, (d) 5 wt.% and (e) 10 wt% (polymer solution concentration=12.5 wt.%, PVA/COS blend ratio=8/2)

The TEM observation reveals the formation of the nanocomposite nanofibers and the distribution of the MMT in the nanofiber matrix. The TEM image in Figure 11 indicates the nanosize MMT in the nanofibers electrospun from the solution containing 0-5 wt.% MMT. It can be clearly observed that each silicate platelet forms a dark line in the nanofiber compare with the pure PVA nanofiber.

The XRD patterns of the PVA/COS/MMT nanocomposite nanofibers are presented in Figure 12. It is well known that, in a nanoclay-polymer composite, unexfoliated or intercalated MMT usually has a peak in the range $3\sim9^{\circ}$ (20). For exfoliated nanocomposites, on the other hand, where single silicate layers are homogeneously dispersed in the polymer matrix, and no distinct diffraction peak in the range of $3\sim9^{\circ}$ (20) should be detected. As shown in Figure 12, as the amount of COS in the PVA/COS blend fibers is increased [(f) to (a)], the diffraction peak at about 19.3° of pristine PVA becomes broad and the intensity of the peak becomes low. Also there is no diffraction peak in $3\sim9^{\circ}$ (20). This suggests that the crystallinity of PVA/COS fibers with higher COS amounts (8/2 and 6/4 mass ratios) is lower in comparison with the electrospun PVA fiber. TEM image (Fig. 11) also confirms that MMT clays are well dispersed in the nanofibers, and they are predominantly exfoliated.



Fig. 12. XRD data of electrospun PVA/COS/MMT nanocomposite nanofibers with diffrent blend ratios and MMT contents

4.2.2 Thermal stability

Thermal stability of electrospun PVA/COS/MMT nanofiber was measured using TGA in nitrogen atmosphere. The TGA thermograms shown in Figure 13 indicate that the nanofiber mats with various PVA/COS mass ratios and MMT contents have different decomposition temperatures. All of the lines show the similar thermogram trend. However, by carefully comparison, it was found that according to mass ratio of COS and MMT, the thermal stability was changed. Higher thermal stability of high MMT content rate might be attributed from its higher chain compactness due to the interaction between the PVA and the clay.



Fig. 13. TGA data of electrospun PVA/COS/MMT nanocomposite nanofibers with 0 and 5 wt.% of MMT contents (polymer solution concentration=12.5%, TCD=15 cm, and applied voltage=15 kV)

4.3 PULL/MMT nanocomposite nanofibers 4.3.1 Morphology and structure property

Both polymer and filler used in this study have hydrophilic character, the modification of MMT for component mixing was not necessary. As was described in literature (Chiellini, 2003), the solution dispersion method of PULL/clay nanocomposite preparation is often used and successful. Such method combined with vigorous stirring was also used in this work to prepare solutions for electrospinning method. Changing the polymer concentration could alter the fiber diameter and morphology very effectively. In a fixed applied voltage (15 kV) and TCD (15 cm), we used 10, 15, 20, 25, and 30 wt.% of PULL solution concentration (Karim et al., 2009). We found that at a 20 wt.% PULL concentration is ideal condition to obtain thinner and uniform PULL nanofibers. It has been obtained a nanometer range of ultrafine electrospun nanofibers (100~500 nm) in aqueous solutions as shown in Figure 14. The diameter of PULL/MMT nanofibers unaffected as well as fibers homogeneity remains identical with increasing of MMT contents from 1 to 10 wt.%. From Figure 15, TEM image supports that the coexistence of MMT clay (dark layers) and PULL matrix (light dark area) for PULL/MMT electrospun fiber mats with 5 wt.% MMT.

The spacing between clay platelets, or gallery spacing, is an indicator of the extent of intercalation/exfoliation of clay platelets within a polymer matrix and can be observed by using X-ray diffraction. Figure 16(A) shows the XRD patterns of as received PULL and MMT, and electropsun PULL/MMT nanofibers with 5 wt.% of MMT contents. Here, the XRD patterns show an intense diffraction peak in 3~9° for electrospun PULL/MMT nanofibers, indicating the possibility of having intercalated silicate the layers of clay dispersed in PULL matrix. There is a broad peak appearing near 19.4°, corresponding to a d spacing of 4.52 for bulk PULL (Biliaderis et al., 1999).



Fig. 14. FE-SEM images of PULL/MMT nanocomposite nanofibers prepared with different MMT contents of (a) 0 wt.%, (b) 1 wt.%, (c) 3 wt.%, (d) 5 wt.% and (e) 10 wt.%



Fig. 15. TEM image of electrospun PULL/MMT nanocomposite nanofibers at 5wt.% MMT

FT-IR spectra give additional information about the structure of nanofibers studied. In Figure 16(B), examples of spectra of as received PULL powder and electrospun PULL/MMT (1, 3, 5, and 10 wt.% of MMT) nanofibers at 400–4000 cm⁻¹ range are shown. Pure PULL exhibits identical bands as shown in Figure 16B(e). In the specific area (1500–650 cm⁻¹) which is characteristic for the pullulan molecule as a whole, the spectra for commercial pullulan as well as those for PULL/MMT electrospun fiber mat samples exhibited similar features. Such

results confirmed the identical chemical structure of the samples. Strong absorption in 850 cm⁻¹ is characteristic of the α -D-glucopiranosid units. Absorption in 755 cm⁻¹ indicates the presence of α -(1 \rightarrow 4)-D-glucosidic bonds, and spectra in 932 cm⁻¹ proved the presence of α - $(1\rightarrow 6)$ -D-glucosidic bonds. Besides, in the areas for reference and evaluated samples the frequencies are analogous (Seo et al., 2004). Bands at 2850-3000 cm⁻¹ are due to stretching vibrations of CH and CH₂ groups and bands attributed to CH/CH₂ deformation vibrations are present at 1300-1500 cm-1 range. Also very intensive, broad hydroxyl band occurs at 3000-3600 cm⁻¹ and accompanying C-O stretching exists at 1000-1260 cm⁻¹. The absorption band corresponding to hydroxyl groups of PULL and MMT (3420 cm⁻¹) was reduced relative to the band of CH stretching vibrations (2930 cm⁻¹) as the interfacial interaction proceeded. Low intensive carbonyl band, is detected at 1724 cm⁻¹ in PULL spectrum and gradually reduced after adding the MMT fillers. All these bands are also present in PULL composites with MMT. The small shifts of absorption maximum and alteration of band shape are results of changes in the nearest surrounding of functional groups. These observations are illustrated in Figure 16 for bands in region 1000-1750 cm⁻¹. Thus, the FT-IR spectroscopy supplied also evidences of possible interactions between PULL matrix and MMT clay, which were suggested above.



Fig. 16. (A) XRD data of as received PULL, electrospun PULL/MMT nanocomposite nanofibers and MMT (B) FT-IR data of electrospun PULL/MMT nanocomposite nanofibers with different MMT contents of (a) 10 wt.%, (b) 5 wt.%, (c) 3 wt.%, (d) 1 wt.% and (e) 0 wt.%

4.3.2 Thermal stability

The PULL/MMT nanofibers melting and crystalline point was investigated by DSC on various MMT contents. Figure 17A shows the DSC thermogram of electrospun PULL/MMT fibers with different mass of MMT contents at a polymer concentration of 20 wt.%. Pure PULL polymer showed a large thermogram peak of melting transition (T_m) at ~ 99 °C. This peak was shifted to 101.4, 102.2, 104.1, and 106.2 °C with the addition of 1, 3, 5, and 10 wt.% of MMT, respectively. The DSC for the nanofibers shows clearly the melting transitions of the PULL, in which there were significant effects of the MMT contents. It was suppressed due to the polymer confinement in accordance with previous work (Strawhecker & Manias 2000). It seems that the inorganic layer affect all polymer morphology also, even though the MMT content was still low with respect to the PULL matrix (Alla et al., 2006).



Fig. 17. (A) DSC data of electrospun PULL/MMT nanocomposite nanofibers with various MMT contents (B) TGA data of electrospun PULL/MMT nanofiber mats with different MMT contents of (a) 0 wt.%, (b) 1 wt.%, (c) 3 wt.%, (d) 5 wt.% and (e) 10 wt.%

Thermal stability of electrospun PULL/MMT nanocomposite nanofibers was measured using TGA in nitrogen atmosphere. Figure 17B shows TGA thermograms of different decomposition temperature with MMT content of 1, 3, 5, and 10 wt.%. The most below

curve of the TGA data represented the bulk PULL i.e. as received PULL powder with no MMT contents and the most upper curve was for mass ratio of 10 wt.% of MMT i.e. the highest mass ratio of MMT content was use in our work. Line (b), (c), and (d) in Figure 17B were displaying three middle mass ratios of MMT contents at the same trend of thermal stability like the line (a) and (e). Within up to 265 °C, there is increased in thermal stability from the pure PULL nanofibers to PULL/MMT (1-10 wt.%) nanocomposite nanofibers. The higher thermal stability of high MMT content rate might be attributed to its higher chain compactness due to the interaction between the PULL and the clay materials.

5. Conclusion

PVA/MMT, PVA/MMT/Ag, PVA/COS/MMT and PULL/MMT nanocomposite nanofibers with aqueous solution are successfully electrospun and characterized by FE-SEM, TEM, XRD, FT-IR, DSC and TGA. Majority of MMT platelets are exfoliated, and they are well distributed within the fiber matrix and oriented along the fiber axis. These exfoliated MMT nanoparticles improved the tensile strength and thermal stability of the electrospun nanofibers. And well dispersed Ag nanoparticles allow nanocomposite nanofibers to have a good anti-bacterial performance, which gives a suggestion for the practical use of a new preservative. The results obtained in this study may help fabricate high performance electrospun polymer nanocomposite nanofibers that can be utilized in many industries such as biomedical application, filter, reinforcement in matrix and protective clothing application.

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Electrodeposition of Metal Matrix Nanocomposites: Improvement of the Chemical Characterization Techniques

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1. Introduction

In this chapter, critical aspects related to the electrodeposition conditions of metal matrix nanocomposite films, from aqueous solutions, are discussed. The efficiency of the use of these films in different technological applications strongly depends on their compositional, morphological and structural characteristics, which are directly related to the preparation method and deposition conditions (e.g. current density, substrate, pH, ions concentration, size and quantity of nanoparticles, electrolyte agitation etc.). Therefore, the correct chemical and physical characterization of nanocomposite coatings is crucial to optimize their synthesis and, thus, their performances. A fast and reliable in-depth chemical characterization of the metallic matrix as well as to evaluate their routine manufacturing quality. The use of direct solid elemental analysis techniques, such as glow discharge (GD), coupled to both optical emission and mass spectrometry provides some unique analytical advantages for the fast analysis of nanocomposite coatings namely to determine nanoparticles concentration, homogeneity and coating thickness.

2. General aspects

Research into the preparation of nanocomposite coatings, by electrochemically codeposition of fine particles with metal from electrolytic solutions, has been investigated by numerous authors. Due to the large number of published works over the last decades, only some review works are cited regarding the state of the art on this subject (Hovestad & Janssen, 1995; Low et al., 2006; Stojak et al., 2001).

Materials are considered nanosized when one of the components dimensions are in the nanometer scale, with typical dimensions smaller than 100 nm. A variety of nanosized particles, ranging from 4 nm to 800 nm diameters, have been successfully incorporated into metallic electrodeposits (Low et al., 2006). These include oxides such as Al₂O₃, ZrO₂, TiO₂ and Cr₂O₃ or carbides like SiC, WC, TiC or nitrides like Si₃N₄ (Bahrololoom & Sani 2005; Jung et al., 2009; Srivastava et al., 2010; Krishnaveni et al., 2008; Stroumbouli et al., 2005; Gay et al., 2001).The metals mostly used are copper and nickel (Low et al., 2006) however other

metals like zinc, silver and, alloys have been used (Gomes et al., 2005; Gay et al., 2001; Tulio & Carlos 2009; Muller et al., 2002; Tian & Cheng, 2007). The most studied system has been the Ni-SiC due to its potential technological applications (Low et al., 2006; Hovestad & Janssen 1995; Benea et al., 2002; Zimmermann et al., 2002; Hou et al., 2002; Garcia et al. 2001; Gyftou et al., 2005; Lekka et al., 2005). Therefore, considering the variety of metals, which can be electrodeposited, electrochemical composite deposition enables the production of a wide range of composite materials that compared to the pure metal coatings have improved physical and (electro)chemical properties (Hovestad & Janssen, 2005). For example, Cualumina and Ni-alumina composite coatings exhibit ultimate tensile strengths, and lower ductility than pure copper or nickel deposits (Lozano-Morales & Podlaha, 2004).

The first application of electrochemically deposited composites dates back to the beginning of the twenty century. Sand particles held by a nickel matrix were utilized as anti-slip coatings on ship stairs (Hovestad & Janssen, 2005). During the 1970s and 1980s, investigations were focused on the need to produce coatings with enhanced mechanical, corrosion and tribological properties. During the 1990s, new areas such as electrocatalysts and photoelectrocatalysts production were emerging, associated with an increasing interest on the particles size. This is due to the higher activity of the semiconducting nanoparticles in comparison with the macro sized particles related to changes on the optical bad gap and surface area (Low et al., 2006). In 2000, Musiani had done a review paper focused on the new applications for the metallic composite materials (Musiani, 2000). Concerning photoelectrochemical activity, the principal application of these materials is strongly linked to the degradation of organic molecules and depends on the high surface-to-volume distribution of the nanoparticles (Tacconi et al. 2000). Although the use of metallic matrix composite electrodes, on the organic pollutant degradation, is still rare, some studies indicate that the metallic matrix has a positive influence on the semiconductor photocatalytic activity (Deguchi et al., 2001). The authors of this chapter are developing, with success, the preparation of photoelectroactive thin films consisting of nanoparticles (TiO₂) dispersed on a metallic matrix (Zn or Zn alloys) suitable to be used as electrode materials for degradation of pharmaceuticals from simulated sewage water (Gomes et al., 2010).

The amount of incorporated particles is the key parameter for the success of metal matrix composite applications, since it largely determines the composite properties such as wear resistance, high-temperature corrosion protection, oxidation resistance and self-lubrication when compared with the corresponding values for pure metal or alloys deposits (Lozano-Morales & Podlaha, 2004; Vaezi et al., 2008). In addition, uniform distribution of codeposited particles within the metal matrix was found to be another crucial parameter (Stankovic & Gojo, 1996; Vidrine & Podhala, 2001). Nevertheless it must be highlighted that the metal matrix morphological and structural characteristics are strongly affected by the particles presence. Furthermore the co-deposition of a sufficient amount of nonagglomerated particles should lead to production of harder and more resistant coatings (Zanella et al., 2009). Particle-reinforced composite coatings based on nickel and alumina are being applied in different technological fields with high demands on friction and corrosion resistance (Jung et al., 2009). Lekka et al. show that the co-deposition of SiC nanoparticles leads to a more noticeable grain refinement and, as a consequence, the nanocomposite deposits present a very high microhardness, 61% higher than pure copper deposits, and an increase of 58% of the abrasion resistance (Lekka et al., 2009).

Future applications of these materials depends on the ability to produce them with controlled composition and properties, using inexpensive and reliable techniques.

Electrodeposition method meets some of these requirements, since it is an economical and versatile technique compared to other preparation techniques. Moreover, it is quickly scaled up to industrial production, offering an inexpensive method to produce large area samples. These are some of the reasons that make this method so popular. In addition, the low processing temperature (around room temperature) minimizes interdiffusion or chemical reaction between the substrate and coating species. The film thickness can be accurately controlled by monitoring the consumed charge and the composition can be tailored by the electrical applied profile and bath composition (Bicelli et al., 2008). The occlusion electrodeposition, or electrochemically co-deposition method, where the particles incorporation occurs simultaneously with the metal ions reduction, uses a precursor bath loaded with the particles to be occluded. This technique is widely used to obtain metal matrix composites due to its ease of preparation, low cost and versatility (Rajeshwar, 2002). The concentration of particles suspended in solution varies from 2 up to 200 g/L producing composites with typically 1-10 vol.% of embedded particles (Stojak et al., 2001).

With the increasing availability of nanoparticles, the interest of the low-cost and low-temperature composite electroplating is continuously growing, with the major challenge being the achievement of high co-deposition rates and homogenous distribution of the particles in the metallic matrix (Gyftou et al., 2008).

Fundamentally, the electrocodeposition process and hence the structure, the morphology and the properties of the composite coatings is affected by the electrodeposition parameters like the electrolysis conditions (composition and agitation of the electrolytic bath, presence of additives, temperature, pH), the electrical profile (Gomes et al., 2005; Fustes et al., 2008) and the particle properties (type, size, shape, surface charge, concentration and dispersion in the bath) (Maurin & Lavanant, 1995; Hovestad & Janssen 1995; Kantepozidou et al., 1996).

3. Theoretical models of metal matrix composite electrodeposition

In a simple way, the particle incorporation in a metal matrix could be described as a fourstep process: (1) formation of surface charge on particles in suspension, (2) particle mass transfer from the bulk of the suspension to the electrode surface, (3) particle-electrode interaction (4) particle incorporation and irreversible entrapment simultaneously with the growing metal layer (Figure 1).



Fig. 1. Some of the steps involved in the metallic matrix composite electrodeposition.

Most of the electrochemical co-deposition mechanisms for the dispersion of inert particles into metallic coatings have been developed for micron-sized particles (Low, 2006). The first model developed was the Guglielmi's model which is based on two steps process involving a loose adsorption and strong adsorption of the particles (Guglielmi, 1972). The first step is a loose physical adsorption of the particles on the cathode, with a high degree of coverage, and without discharge of the electro-active ions adsorbed on the particles. The fractional coverage follows a Langmuir adsorption isotherm. The second step is the strong electrochemical adsorption of the particles, caused by the applied electrochemical field, accompanied by the discharge of the electro-active ions. Both steps take place at the same time all over the cathode surface. If a particle is strongly adsorbed on the cathode, it will be embedded in the growing metal layer by the electrodeposition of free solvated electro-active ions from the plating bath (Jung et al., 2009; Tian & Cheng, 2007).

From this model the volume fraction of incorporated particles, α , can be mathematically expressed by:

$$\frac{\alpha}{1-\alpha} = \frac{zF\rho_m V_o}{M_m i_o} \cdot e^{(B-A)\eta} \cdot \frac{kc_{p,b}}{1+kc_{n,b}}$$
(1)

where M_m and ρ_m are the atomic weight and the density of electrodeposited metal respectively, i_0 the exchanging current density, z the valence of the electrodeposited metal, F the Faraday constant, η the electrode reaction overpotential, $c_{p,b}$ the particle concentration in the bulk electrolyte and k the Langmuir isotherm constant, mainly determined by the intensity of interaction between particles and cathode. The parameters V_0 and B are related to particle deposition, and both play a symmetrical role with the parameters i_0 and A related to metal deposition (Wang & Wei, 2003). The validity of Guglielmi's model has been verified with different deposition systems, such as SiC and TiO₂ particles with nickel from sulfamate bath (Guglielmi, 1972), or α -Al₂O₃ particles with copper from a copper sulfate plating bath (Celis & Roos, 1977; Lee & Wan, 1988).

However the model neglects hydrodynamics, particle size and ageing effects what is its main drawback (Jung et al., 2009).

The model developed by Celis (Celis et al, 1987) uses probability concept to describe the amount of particles that can be incorporated at a given current density and assumes that five steps are involved into the incorporation of the particles: (1) formation of an ionic cloud around the particles; (2) transport of the particles by convection to the hydrodynamic boundary layer; (3) transport of the particles by diffusion to the cathode; (4) free ions and electro-active ions adsorbed on the particles are adsorbed at the cathode, and (5) electrochemical reduction of the absorbed ions at the cathode with the embedding of the particles into the growing metallic matrix.

This model was satisfactory used for the Cu-Al₂O₃ and Au-Al₂O₃ systems. Later on Fransaer proposed another model (Fransaer et al., 1992) that was developed to non-Brownian particles, particles with a diameter bellow 1 μ m, involving two steps: (1) reduction of metal ions (described by Butler-Volmer expression) and (2) co-deposition of particle (described by trajectory expression). This model has been used successfully on the qualitatively explanation of experimental data for Zn-polystyrene composite depositions. From a mechanistic point of view, this trajectory model offers a very good description for getting a better insight into composite deposition. Nevertheless the particle-electrode interaction forces and their relative importance remain a point of discussion. Another contribution in

this area is the model of Vereecken (Vereecken et al, 2000) that takes into account the particles kinetics and residence time at the electrode surface. The transport of particles to the surface is controlled by convective-diffusion. The influence of particle gravitational force and hydrodynamics is accounted for various current densities. It is valid only when the particle size is smaller than the diffusion layer thickness. The authors show that incorporation of 300 nm Al_2O_3 particles into nickel films can be well described by this model. More recently Lee and Talbot (Lee & Talbot, 2007), proposed a model to predict the amount of nanoparticle incorporation in a kinetically as well as in the mass transfer limited region of the electrochemical deposition which agrees well with the experimental data of the Cu-Al₂O₃ system.

Currently, the models used to describe the inclusion of particles are restricted to specific conditions, so empirical laboratory trials remain very important. Future models, describing the co-deposition process, will require special attention to interactive variables such as the nanoparticle characteristics (composition and crystallographic phase, size, density, and shape) and the operating electrolysis parameters. The validity of the various theoretical models, underlying particle incorporation in a metal matrix, still requires attention, since the electrochemical co-deposition is still not fully understood (Low, 2006; Vidrine & Podlaha, 2001).

4. Particle characteristics

Nanocomposite coatings have been studied increasingly in the last 10 years. However the results are often contradictory and inconsistent and they are, therefore, difficult to compare with micro-composites (Medeliene, 2002; Malfatti et al., 2005; Zanella et al., 2009). The mass transport of the inert particles towards the cathode surface is a crucial factor in determining the extent of their occlusion within the growing metallic matrix (Zhou et al., 1997). The particle electrode interaction depends on the particle surface properties, which are determined by the particle type, bath composition, pH and metal surface composition.

For some systems like Ni-SiC, the two-step co-deposition mechanism proposed by Guglielmi is valid. In addition the results show that the ultra-fine SiC is more difficult to co-deposit than the coarse SiC, and the rate determined step is controlled by the transferring process of loose adsorption to strong adsorption (Wang & Wei, 2003). With the same quantity of powder in the bath, the embedded micro-powder content is about 25–30 wt % while the nano-powder content is always less than 1 wt % (Zanella et al., 2009; Shao et al., 2002).

The smaller the particle the most important are colloidal forces (van der Waals, electrostatic attraction/repulsion and hydrophobic/hydrophilic interaction forces). The most difficult to quantify are the hydrophobic/hydrophilic interaction forces, as no general theory describing such forces may be found in the literature (Socha et al., 2004).

Particles dispersed in a continuous electrolyte solution are in constant Brownian motion. When two particles approach one another, the energy existing between the particles determines whether the particles will separate or agglomerate. Generally, particle agglomeration occurs when larger attraction than repulsion energy exists between them. The magnitude of the net forces involved, in producing an agglomerated structure, clearly depends on the conditions and the nature of the system. The knowledge of the interfacial region structure is an important factor in order to understand the dispersion stability of solid particles within the electrolyte (Kuo et al., 2004).

At higher ionic strength of the electrolyte or lower particle charge, the particles may agglomerate irreversibly. If the ionic strength increases, the agglomeration of the particles increases too. However if the state of agglomeration is reversible it can be easily turned into the dispersed state by mechanical stirring. Repulsive forces can be tuned via experimental conditions as pH, ionic strength, etc. The zeta potential, which is a quantitative measure for the particle surface charge, gives an indication of the stability of the colloidal system. As consequence, a higher zeta potential induces a lower degree of particle agglomeration producing a higher concentration of non-agglomerated particles in the electrolyte (Simunkova et al., 2009). In electrocodeposition the stability of the colloid dispersion is mandatory, since the particles shall be preferentially incorporated in the form of individual particles in order to improve the particle incorporation and as consequence the composite properties. Simunkova et al. show, for the nickel composites, that as electrostatic repulsion within the dispersion increases, particle agglomeration slows down and the concentration of non-agglomerated particles rises resulting in an enhanced amount of particles incorporated in the electroplated Ni layers (Simunkova et al., 2009). Effective particle dispersion in the electrolyte solution creates more opportunities for loose particle adsorption onto the electrode. Smaller agglomerated particle groups have a higher attraction force from the electric field that produced effective adsorption (Kuo et al., 2004).

The zeta potential of nano- and micro-scaled particles is influenced by many factors, such as the source of particles (variable preparation and stabilization), the treatment with different surfactants, the electrolyte concentration (ionic strength), the particle morphology and size, the pH of the solution, and the state of hydration (Moreno et al., 1988; Wernet & Feke, 1994; Morterra et al., 1994; Leong et al., 1995; Kim et al., 1998; Kagawa et al., 1987).

The particles always interact with the electrolyte and therefore chemical and physical adsorption of electrolyte ions onto the particle occurs. This adsorption and the initial particle surface composition determine the particle surface charge, which induces a double layer of electrolyte ions around the particle. In electrolytes double layers play a major role in the interactions between particles and also between particles and the electrode (Hovestad & Janssen, 2005). In aqueous media, the oxide particles, due to protonation– deprotonation of the superficial groups can change their surface charge depending on the solution pH (Simunkova et al. 2009) according to:

 $\text{M-OH} + \text{H}^{+} \rightarrow \text{-M-OH}_{2^{+}}$

 $-M-OH + OH^{-} \rightarrow -M-O^{-} + H_2O$

For example the TiO₂ point of zero charge (pzc) is ca 6.0, thus for pH values lower than 6.0, the positively charged TiO₂ particles would be expected to be electrostatically attracted to the cathode surface, thus assisting in their solution transport via migration. On the contrary, at solution pH values higher than the pzc, the TiO₂ particles would be negatively charged and thus repelled from the cathode surface (Zhou et al., 1997). For the Ni-TiO₂ system, the experimental data revealed that co-deposition of TiO₂ nanoparticles is favoured at low pH values and current densities, implying that there is a plentiful adsorption of H⁺ on the titania surface. As the particle surfaces become positively charged they will be strongly adsorbed on the cathode leading to an enhanced electrolytic co-deposition (Spanou et al., 2009).

Nevertheless, in some published works, it is pointed out the electrodeposition of negatively charged particles into Ni matrix with success. These findings are in contradiction with the traditional theory of particles transport towards the cathode by means of electrophoresis (Low et al., 2006). This might be correlated to the absolute value of the zeta potential. This factor is very important for the degree of incorporation and not only the polarity of the zeta potential as mentioned previously.

According to the model developed by Bund and Thiemig, negatively charged particles are preferentially attracted by the positive excess charge in the electrolytic part of the electrode electrical double layer. When the particle comes closer to the electrode, the shell of adsorbed ions on the particle is stripped off, within the electric double layer and the particle becomes incorporated into the growing metal layer (Bund & Thiemig, 2007).

As general accepted the transport of the particles to the cathode surface occurs by electrophoresis, mechanical entrapment, adsorption and convective-diffusion mechanisms (Low et al., 2006). Electrolyte agitation is usually necessary to maintain the particles in suspension and to transport the particles to the electrode surface. Vaezi et al. have verified that increasing the stirring rate up to 120 rpm causes the increase of the percentage of incorporated SiC nanoparticles but when the stirring rate is too high, a decreasing trend of the weight percent is observed, principally caused by the collision factor. At a high-stirring rate, because of the turbulent flow in the bath, the SiC nanoparticles on the cathode surface are washed away and thus the SiC nanoparticles percentage in the composite coating decreases. It was assumed that increasing the stirring rate, increases the forces acting on the nanoparticles, resting on the cathode surface, decreasing the weight percentage of the SiC nanoparticles in the composite coating (Vaezi et al., 2008).

The co-deposition of nanoparticles during electrochemical deposition of a metallic film depends on the rate of the metal deposition and on the flux of particles to the film surface which is strictly related with the applied electric profile. The growth rate of the metal film is determined by the deposition current density.

Generally, the strong adsorption is the rate-determining step of the electrodeposition process because it is more difficult to occur than the loose adsorption. The strong adsorption can be promoted by high overpotential corresponding to increasing current density. As a result, the particle content in the coatings increases with increasing current density. Nevertheless, at higher current density, the improvement of metal deposition rate caused by the increase in current density exceeds the promotion effect of particle incorporation, which leads to the decrease in the particle content (Guo et al., 2006).

The relationship between cathodic current density and incorporation rate, for different particle concentrations in the bath, has been studied by Gay et al.. It was concluded that for low current densities (0.5 A dm⁻²), the incorporation rate is very weak <2% and for higher current densities (1.5 to 2 A dm⁻²), the coatings appear rough. In these latter cases, the incorporation rate is still very weak (approx. 1%) whatever the plating bath concentration is (Gay et al., 2001).

Studies on the Ni-TiO₂ system done by Aal et al. show that the wt. % of co-deposited TiO₂ increases with current density. According to the Stokes model, assuming that the colloidal particle is sphere-shaped, the electrophoretic velocity (V_E) under an electric field (E) can be expressed by:

$$V_E = \mu_E E = \frac{q}{6\pi\eta r} E \tag{2}$$

where μ_E is the electrophoretic mobility, q the particle charge, r the particle radius , and η the viscosity of the suspension. Considering this, the increase of the current density accelerates the electrophoretic velocity of the TiO₂ particles and increases the Coulombic force between the Ni²⁺ adsorbed on the particles and the cathode which consequently increases the TiO₂ content in the Ni deposit (Aal & Hassan, 2009). Similar behavior was revealed for the Ni-SiC composites (Wang & Wei, 2003).

Otherwise, it has been observed that the amount of embedded SiC particles increases with both increasing concentration of suspended SiC particles and additives' presence in the electrolyte (Gyftou et al., 2008). Indeed the particle loading in suspension is a very important parameter. At low loadings, co-deposition is limited by the supply of particles to the electrode. As the particle loading increases, so does the incorporation level. But at the highest loadings (beyond which particle settling becomes significant), the increase in incorporation is not proportional to the increase in loading and a constant value is attained (Stojak et al., 2001).

In many cases the enhanced performance of the composite film is mainly caused by a change in the metal matrix growth mode or crystallite size and not so much by the presence of the particles themselves. In general the crystallite size of the metal matrix decreases due to the presence of the nanoparticles in the electrolyte. For instance the crystallite size of the nickel matrix was reduced from 115 to 30 nm due to the presence of 120 g/L alumina nanoparticles. Some studies have focused on the particle effect on the metal reduction rate and the conclusions are in somehow contradictory (Lozano-Morales & Podlaha, 2004). Few works have shown that there is no change in the metal deposition rate with particle addition to the electrolyte. Lozano-Morales et al. show, for Cu-Al₂O₃ nanocomposites, that, at a particle loading of 12.5 g/L, there is no change in the kinetic behaviour whatever the rotation rate is. However, the Cu reduction is inhibited, in kinetically limited region, when 39 g/L particles are added. Under mass-transfer control, the limiting current density remained the same at low particle loadings and was enhanced for higher particle concentrations (Lozano-Morales & Podlaha, 2004).

The cathodic polarization curves for the deposition of the Ni-SiC composites containing different concentrations of SiC nanoparticles are shown in Figure 2.



Fig. 2. Cathodic polarization curves for the deposition of Ni–SiC at different concentrations of SiC nanoparticles in the bath (Vaezi et al., 2008). (Reprint with the permission from Elsevier Limited)

It is clear that the addition of SiC nanoparticles to the electrolyte, shifts the reduction potential of nickel towards larger negatives values, but the slope of the curve keeps unchanged. This shift is attributed to a decrease in the copper cathode active surface area, owing to the adsorption of the SiC nanoparticles, and may also be related to the decrease in the ionic transport by the SiC nanoparticles, which does not significantly affect the electrochemical reaction mechanism (Vaezi et al., 2008). By contrast Benea et al., found for

the same system that the addition of SiC nanoparticles displaces the nickel reduction curve (Figure 3) to more positive potentials. The shift in the reduction potential was attributed to an increase in the active surface area due to the adsorbed particles on the nickel cathode and to a possible increase in ionic transport by the nanoparticles (Benea et al., 2002).



Fig. 3. Cathodic potentiodynamic diagrams for electrodeposition of nickel in presence and absence of SiC nanoparticles. Sweep rate is 0.5 mV/s (Benea et al., 2002, a). (Reprint with the permission from Elsevier Limited)

The lack of reproducibility shown by these two results could be correlated to the different deposition conditions used namely, cathode nature, particle size, solution pH and temperature.

In addition, the metal deposition rate, determined by average current density, have a huge influence on the particle content of the coatings as mentioned before (Guo et al., 2006).

5. Pulse plating methodology

Various electrodeposition techniques namely pulsed current, pulsed reverse current and pulsed potentiostatic can be employed to improve the incorporation of nanoparticles into metal matrix (Jung et al., 2009).

Several published studies have proved that the application of pulsed current (PC) technique in nickel electroplating results in the production of composite deposits with enhanced mechanical properties, higher percentages of incorporation and more uniform distribution of the particles in the metallic matrix than those attained by direct current (DC) technique (Stroumbouli et al., 2005).

Electrochemical deposition by pulsed current, is a very versatile method, since apart from the type, shape and amount of dispersed particles in the electrolyte, the composite properties can be optimized by the variation of the electrodeposition parameters such as current density, duty cycle and pulse frequency. The formation of deposits with desired composition, structure and porosity can be promoted by an adequate choice of these parameters (Chandrasekar & Pushpavanam, 2008).

The pulsed current parameters are the pulse length t_{on} , the time between two pulses t_{off} , the pulse height i_p and the average current density i_A , (Figure 4) defined as:

$$\mathbf{i}_{A} = (\mathbf{i}_{p} \cdot \mathbf{t}_{on}) / (\mathbf{t}_{on} + \mathbf{t}_{off})$$
(3)

The duty cycle is the ratio of pulse length (on-time) and the sum of on- and off-time and frequency is the inverse of the sum of t_{on} and t_{off} . The imposed pulse height causes the depletion of ions near the cathode. During t_{off} , ions migrate to the interfacial region and when t_{on} comes after the end of the first cycle, the repeating of the cycles occurs.



Fig. 4. Typical pulse-current waveform (Chandrasekar & Pushpavanam, 2008). (Reprint with the permission from Elsevier Limited)

By modifying these parameters changes on the cathodic overvoltage may occur, which affects the rate and activation energy of nucleation. At a given average current density, a decrease on the metal crystallite dimensions, with the decreasing of t_{on} , when followed by a short t_{off} , have been reported. These results have been assigned to an increase of the number of crystal nucleus formed (Bicelli et al., 2008). In addition longer t_{off} promotes the arriving of more particles near the cathode and consequently a higher number of particles are incorporated. Therefore pulse plating techniques are very important for the tailoring of nanocomposites.

In the case of Ni- SiC co-deposition, the application of pulsed current techniques results in the production of composite coatings with higher percentages of incorporation, reduced crystallite sizes and a more uniform distribution of SiC particles in the Ni matrix than those achieved under direct current regime (Gyftou et al., 2008).

In the pulsed-reverse current technique (PRC) a stripping time is introduced into the plating cycle, during which the metal surface protrusions selectively dissolves, what ensures a more uniform deposit (Chandrasekar & Pushpavanam, 2008). Comparing the PRC with the direct current method: (1) the amount of nanoparticles in a metal deposit can be enhanced, (2) a lower concentration of nanoparticles in the electrolyte solution can be used and (3) selective entrapment of nanoparticles with similar sizes can be achieved (Low, 2006). These features make this technique most adequate for the preparation of composites, enabling an increase of the particle incorporation in the metal matrix. Studies on the preparation of Zn-TiO₂ nanocomposite using the PRC technique have shown an improvement on the TiO₂ content in the nanocomposite (Fustes et al., 2008).

In general, for pulse plating and pulse reverse plating, high amounts of incorporated particles were found at low values of the average current density (Thiemig et al., 2007). On the other hand, various authors assumed that the duty cycle and pulse frequency affect the volume percentage of incorporated particles in the coatings. It is interesting to note that the influence of the duty cycle on the amount of incorporated particles is much bigger than the effect of the pulse frequency. These results indicate that when the pulse off-time is longer, i.e. at low duty cycles, more particles are incorporated into the coating, due to continuous agitation, with renovation of the bath composition near the cathode. It seems that the duty cycle, has a greater influence on the amount of incorporated particles than simply the length of the off-time, indicated by pulse frequency (Bahrololoom & Sani, 2005). This effect is illustrated in figure 5 for the Ni-ZrB₂ system. Moreover, in a study of pulse plating nickel-alumina composite coatings, Bahrololoom and Sani investigated both the effect of the duty cycle and frequency together, increased the composites' wear resistance in the same way that pulse parameters influence their hardness (Bahrololoom & Sani, 2005).



Fig. 5. Effect of the pulse frequency with 50% duty cycle and the duty cycle with 500 Hz frequency on the volume fraction of embedded ZrB_2 particles at an average current density of 5 A dm⁻² (Guo et al., 2006). (Reprint with the permission from Institute of Metal Research)

At constant average current density, a lower duty cycle means a higher peak current density. Consequently, as showed previously, the strong adsorption of particles is improved by high overpotentials (Yeh & Wan, 1994). At high current densities, metallic ions are transported faster than the particles, which are transported by the mechanical agitation. Hence, the co-deposition of particles becomes particle-transfer controlled. Besides, at higher current densities the particles do not have enough time to be loosely adsorbed on the electrode surface and, as a consequence, a lower level of incorporation of the particles is obtained. In addition, at higher current densities, the hydrogen bubbles generated at the cathode surface, tend to attract the particles and prevent them from co-deposition in the metal matrix (Krishnaveni et al., 2008).

6. Characterization techniques

The relationship between the nanocomposite characteristics, synthesis conditions and properties must be well established since it affects future applications of these materials.

Modifications on the composition, namely, the amount and distribution of the incoporated nanoparticles, structure and morphology of the nanocomposite films induced by changes on the deposition conditions must be properly evaluated by the analysis of the bulk and surface characteristics of the deposit.

To reach this objective X-ray diffraction (XRD), scanning electron microscopy coupled with energy dispersive X-ray spectroscopy (SEM/EDS), atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS) and electrogravimetric analysis are ex-situ characterization techniques usually used.

From the XRD characterization technique it is expected to obtain information mainly about metallic matrix, namely, the crystal structure, texture and matrix crystallite size. Although the presence of particles can also be detected. The metal crystallites size is usually determined from the broadening of the strongest XRD reflection according to Scherrer equation (Cullity, 1978).

The preferred orientation of the zinc electrodeposits has been estimated from the X-ray data according to the methodology developed by Bérubé (Bérubé & L Espérance, 1989), where the texture coefficient (T_c) is calculated by using the equation (4):

$$T_{c} = (I_{(hkl)} / \sum I_{(hkl)}) \times (\sum I_{p(hkl)} / I_{p(hkl)})$$
(4)

where $I_{(hkl)}$ is the diffraction line intensity of the (hkl) reflection of metal electrodeposits and $\Sigma I_{(hkl)}$ the sum of the intensities of all the diffraction lines monitored. The index p refers to the reference metallic powder sample. A value of T_c greater than 1 indicates a preferred orientation of the (hkl) reflection compared with the random distribution of the grains in the reference metallic powder. This methodology gave good results for nanocomposites with Ni or Zn matrixes (Thiemig & Bund, 2008; Fustes et al., 2008).

The most important conclusion from the published data is that the solid particles, present in the solution exert strong influence on the texture of the growing metal layer, even if they are not embedded in the metal. Considering the electrodeposition of Ni-SiC, Gyftou et al. have concluded, from the study of the textural perfection of the deposits, that the presence of nanoparticles led to the worsening of the quality of the [1 0 0] preferred orientation, observing a mixed crystal orientation through [1 0 0] and [2 1 1] axes when high concentration of embedded particles were used (Gyftou et al., 2008).

Some authors (Spanou et al., 2009) assume that the modification of metallic orientation in addition to the decrease of crystallite size point to an effective incorporation or embedding of the particles. In accordance with this, the embedding SiC nano-particles in a Ni metallic matrix resulted in the deposition of composite with smaller crystallite sizes and more structural defects than those of pure Ni deposits (Gyftou et al., 2008; Angerer et al., 2009). In a qualitative approach Fustes et al. used the XRD to correlate the amount of TiO_2 in the Zn- TiO_2 coatings with the particles concentration in solution (Fustes et al., 2008).

Concerning the morphology and elemental composition of the surface and cross-over sections the composites are, in general, analysed by SEM/EDS. This analysis of the codeposited layers are performed in order to characterise the coating morphology, to confirm particle incorporation and estimate the particle distribution in the layer (Simunkova et al., 2009). The deposits surface roughness is usually affected by the presence of particles in suspension. In general, composite coatings are considered to be rougher than the particle-free coatings due to the entrapment of particles (Krishnaveni et al., 2008). Investigations of nickel dispersion coatings cross sections were carried out by Bahrololoom and Sani in order to clarify the composition and qualitative particle distribution induced by modifications of the duty cycle and frequency values (Figure 6). The authors had concluded that the amount of particles could increase due to the variation of these parameters without any modification in the other electrodeposition conditions.



Fig. 6. Photomicrographs of the cross sections of nickel–alumina composite coatings electrodeposited with an average pulse current density of 5 A dm2 and at various pulse duty cycles and frequencies. (a)- 20% duty cycle and 50 Hz frequency, (b)- 80% duty cycle and 50 Hz frequency, (c)- 60% duty cycle and 20 Hz frequency, (d)- 60% duty cycle and 80 Hz frequency (Bahrololoom & Sani, 2005). (Reprint with the permission from Elsevier Limited)

Other authors like Erler et al. used the cross-section technique to gain information of the particles distribution through the Ni-TiO₂ coating. They showed that the particles are not uniformly distributed, in view of the fact that there is an "initial layer with no or very few particles", whatever the particle type is. At the initial stage, super-saturation of nickel atoms adsorption and three-dimensional nucleation can occur only on the substrate particle-free areas. Therefore, a particle free metallic layer has to be deposited by the growth of the initial crystals. Next the particles can stick to the "rough" nickel surface and will be overgrown. The proportion of incorporated particles increases and reaches a stationary value (Erler et al., 2003). The particles distribution gradient in the metallic deposit can be intentionally achieved in a single electrolyte bath by the simple alteration of the applied current density or potential and/or by modulation of the particles hydrodynamics and concentration in the solution (Low et al., 2006). AFM analysis provides available surface morphology characterization at the nanometric scale and due to high resolution imaging, surface roughness values can be estimated (Gomes et al., 2005; McCormack et al., 2003). Tu et al. have investigated by XPS the interaction between Al_2O_3 or SiO₂ nanoparticles and a nickel metal matrix. They have concluded that there is not only a mechanical connection, but also a chemical combination between the nanoparticles and the nickel matrix, at the interface, in the composite coating (Tu et al., 2008).

Besides the qualitative characterization, the quantification of the amount of co-deposited nanoparticles is also a very important issue and could be accomplished by several techniques such as SEM, EDS, induced coupled plasma spectroscopy (ICP), glow discharge (GD) spectrometries and other chemical analysis methods.

In order to determine the amount of incorporated alumina in Ni composites, Jung et al. have measured the density of composite samples using Helium pycnometry. This is a nondestructive method that does not require special sample geometries, an advantage in relation to gravimetric methods. Due to the large difference in density between the nickel matrix and the incorporated alumina particles, the particles volume fraction in the composites could be evaluated after a mathematical treatment of the experimental data (Jung et al., 2009).

In 1977, Celis et al., used atomic-absorption spectrometry to determine the amount of alumina in a copper matrix and have shown that this technique can be applicable "with reasonable accuracy" down to 0.02 wt% for 1 g samples (Celis et al., 1977). More recently ICP technique was used to estimate the amount of TiO_2 in Zn- TiO_2 composites (Deguchi et al., 2001; Frade et al., 2010). However, it is a rather tedious and time consumption approach, since in most cases the sample has to be dissolved. Moreover, no information about particles distribution is obtained (just averaged composition).

Considering the EDS analysis, the measurements can be performed both on the surface as well as in the cross section of the composite films. The EDS analysis domains should have well defined size and, at least, three points chosen randomly should be used for the estimation of an average value (Bund & Thiemig, 2007). The wt% average value, as obtained, is variable and depends on the considered system and the deposition conditions, as referred previously. It must be noticed that currently this is one of the most used methodology for the quantitative analysis though it is only appropriate for semiquantitative analysis due to technical limitations.

In the literature, there is little discussion of the accuracy or reproducibility of the analytical techniques used for determining the corresponding matrix and particle composition. Hence, an accurate and reproducible analytical method is needed for verifying the particle incorporation and distribution. Although the effects of the process variables, of which many are interrelated, can also vary for different particle-electrolyte systems and electrodeposition conditions used (Stojak et al., 2001).

Nowadays GDs are used for depth profile analysis in many different fields. In fact, GDs are implemented as routine technique for quality control in many industries (steel, aluminium, car-manufacturing, etc) and as a valuable tool in materials science. GDs are being used to reveal processes at the surface (e.g. passivation on highly corrosion-resistant stainless steel), as well as to understand the behavior (tribological properties, corrosion, diffusion processes, etc) of surface treatments such as physical or chemical vapour deposition or ion implantation (Bayón et al., 2010). Moreover, GDs have demonstrated their capabilities to assist the improved synthesis of specialized materials, including glass coatings (Muñiz et al., 2008), biomedical implants (Kern et al., 2006), photocatalyzers (Yuksel et al., 2009), thin films for the photovoltaic (Sánchez et al., 2010) and microelectronic industries (Schwaller et al., 2006). The emerging impact of glow discharges (GDs) either coupled to optical emission spectrometry (OES) or mass spectrometry (MS) for practical surface and thin film analysis is based on many proved remarkable features, including high depth resolution, multielement capability, low detection limits, minimal matrix effects, accurate quantification,

comparatively low price, easiness of use and high sample throughput. Though GDs had been mostly known as powerful analytical tools for depth profiling analysis of relatively thick films (microns range) such as galvanized steels, in recent years they have demonstrated a good performance also for depth profile analysis of thin films. It had been traditionally considered that analytical information from the outermost surface regions of the solid sample was inaccessible by GD-OES and GD-MS due to the rather unstable discharge often observed at the beginning of each analysis. However, instrumental improvements and development of proper operation methodologies have completely changed this picture and examples demonstrating the analytical potential of GD devices for ultra-thin film analysis (less than 10 nm thick) have emerged during the last few years (Fernandez et al., 2010).

Provided that the sample is compatible with vacuum, GD-OES can analyse practically any solid material (Marcus & Broekaert, 2003). The formation of a GD takes place in a low pressure chamber through which a gas (usually high purity argon) is continuously flowing. The device consists of a grounded anode and a cathode (the sample). A potential breaks down the discharge gas, yielding Ar ions which are attracted towards the sample. By the process of sputtering, atoms, electrons and ions are liberated from the sample and through collisions in the plasma the atoms from the analyte are excited and ionized (see Figure 7). Therefore, GDs allow the generation of analytical information from a sequential two-step process: first, the analytes are sputtered from the solid material producing a crater with a diameter of a few mm (so, it is a destructive technique). Next, the sputtered atoms are excited and ionized in the discharge (thus allowing for OES or MS detection) giving rise to an extremely rapid technique for bulk and depth profiling analysis. The most common mode of operation in GD spectroscopy is the application of a direct current (dc) voltage. The dc-GD has demonstrated to be a rapid and easy-to-handle technique for the elemental analysis of electrically conducting samples; unfortunately, the dc mode is restricted to the direct analysis of conducting materials. The use of radiofrequency (rf) powered GDs has tremendously increased the application field due to their ability to sputter both conducting and insulating materials. The analytical similarities between rf- and dc-GDs indicate that any quantitative schemes developed for dc-GDs could be extended to the other one, and the main differences is the choice of the experimental control parameters in each discharge.

Using dc-GDs three key parameters should be considered: pressure in the discharge chamber, voltage and electrical current. These parameters are interdependent and when fixing two of them no choice for the selection of the third one is left. Working with rf-GDs, there are also three operating parameters which can be controlled: discharge pressure, dc-voltages developed at the sample and rf-generator output power. For conductive samples, the dc bias potential and the applied potential are closely related, so, in this case to measure the applied rf potential is accurate enough. However, at present this is not so easy for non conducting samples in commercially available instruments. Therefore, the experimental operating conditions of analysis for insulators by rf-GD must usually be defined by fixing the applied rf-power and pressure.

Further, GD devices have been traditionally operated in a continuous mode providing a steady-state population of sputtered atoms. However, the GD can be also operated in a pulsed mode (dc and rf) wherein each pulse generates a packet of sample atoms (Belenguer et al., 2009). A pulsed GD is created by periodically applying a pulse of high power during milliseconds or even microseconds. During each pulse, an atom/ion packet from the surface material is generated and will expand along the discharge chamber. Pulsed GDs allow an



Fig. 7. Basic processes and instrumentation in glow discharge - optical emission and mass spectrometry

additional way of controlling the plasma by selecting the pulse parameters (e.g. pulse and period lengths). For example, high instantaneous powers can be applied without sample thermal degradation by just varying the duty cycle of the pulses, giving rise to higher instantaneous signals of analyte ions/photons than the steady state discharge. However, in average the sputtering rate is much lower and so pulsed GDs offer a great potential for ultra-thin layers. Moreover, different discharge processes take place at different times within a single pulse and this allows, when coupled to a mass analyser with a time resolved signal acquisition spectrometer such as the TOF (time of flight), to obtaining quasi-simultaneous structural, molecular and elemental information from the sample (Fliegel et al., 2006).

It is known that emission and ionization yields are also affected by small amounts of hydrogen (Weyler & Bengtson, 2010) and, in general, by light elements (C, N and O) in the plasma, coming either from contamination of the plasma gas (Ar) or from the specimen sputtering (i.e. sample constituents). Thus, correction algorithms should be used in such cases. Moreover, the presence of various species of gaseous elements originated from adsorbed gases and contaminants (such as H₂O, C-H compounds) should be most carefully taken into account for thin film analysis. As a result of the pre-vacuum technology required in GD instruments, serious contamination by water and hydrocarbons can be found in GD sources. Such contaminants disturb a fast achievement of the needed balance in the plasma and, moreover, the experimental results could be misinterpreted. Such disturbing influence of contamination on the GD analyses is generally reduced by adopting different strategies (which can be combined), including: (i) reduction of gas adsorption and increase of gas desorption before every measurement (e.g. by very quick sample change and venting with a

clean noble gas at pressures slightly higher than the ambient atmospheric pressure and by evacuation with high pumping speed and an increase of the source temperature, respectively); (ii) pre-sputtering with a piece of monocrystalline silicon (the sputtering of sacrificial material is undertaken under conditions similar to those used for the analysis of the sample, being in this manner the inner surfaces of the anode covered with this low-out gassing coating) (Inayoshi et al., 1999); and (iii) use of a low energy plasma to allow for a soft cleaning of the specimen surface prior to the analysis (Molchan et al., 2009), mainly removing contaminants from the surface of the target material.

For depth profile analysis, "analyte concentrations *versus* sample depth profile" (quantitative profiles) are frequently required. Thus, the "measured elemental signal intensities *versus* time profile" (qualitative profiles) experimental curves have to be transformed by means of adequate algorithms and such transformation requires proper calibrations. In principle, this conversion could be difficult mainly due the unavoidable variations of the main sample constituents along the analysis time, which give rise to changes in the electrical discharge conditions. Fortunately, a most interesting feature of GDs is the low matrix effects observed which allow for rather simple quantification schemes.

Concerning the characterization of nanocomposite films by GD sources, few attempts have been performed during the last decade, mainly using GD-OES. For Zn-TiO₂ nanocomposite films on steel with thicknesses of 10-15 μ m, prepared from a ZnCl₂-based bath, GD-OES was successfully used to optimize the preparation conditions (Deguchi et al., 2001). Figure 8 shows the qualitative depth profile obtained by GD-OES for two TiO₂-Zn nanocomposite films prepared at different conditions. Depth profile observed in Figure 8b shows that a small amount of TiO₂ particles is present only near the surface of the film, whereas in Figure 8a Ti is distributed throughout the film and its signal intensity remarkably increases as it approaches the surface. Thus, it should be highlighted that GD-OES allow us to clarify that the synthesis TiO₂ particles are incorporated throughout the film and the loaded amount increases near the surface.

GD sources can be employed for the characterization of different types of nanocomposite films like Ni-SiC nanocomposite (Lekka et al., 2010) giving GD-OES information about the metallic matrix thickness and the amount and distribution of the particles through the film.

Additionally, GDs sources can be employed as a complementary technique to scanning electron microscopy (SEM) for the characterization and optimization of synthesis procedures of Ni-Zn-TiO₂ nanocomposites (Fernández et al., 2010). Figures 9a and 9b show SEM images obtained for Ni-Zn-TiO₂ nanocomposite films deposited onto steel substrates by electrodeposition in sulphate and chloride solutions. As can be seen, depending on the bath conditions the surface morphology is different: metallic grains with different shapes and sizes were observed using sulphate and chlorine baths. Qualitative profiles obtained by GD-OES for the two synthesis conditions are collected in Figures 9c and 9d, showing valuable information. In both cases, it is possible to discriminate the Ni-Zn-TiO₂ film from the steel substrate and a homogeneous distribution for Ni, Zn and TiO₂ along the coating were observed. However, Zn and Ti were more homogeneously distributed for the sulphate medium as well as better defined interface and a higher thickness of the film were also obtained.

Therefore, this analytical tool offers a tremendous interest to assist the synthesis optimization process as well as for the quality control of nanocomposite films in a wide variety of applications.



Fig. 8. GD-OES depth profiles for the TiO₂-Zn nanocomposite films prepared at I_d = 12 A dm⁻².A) TiO₂-Zn(0.3,100)/Steel; B) TiO₂-Zn(0,100)/Steel (Deguchi et al., 2001). (Reprint with the permission from Springer)



Fig. 9. Characterization of Ni-Zn-TiO₂ nanocomposite films deposited onto steel A & B) SEM images in sulphate and chloride baths, respectively C & D). Qualitative depth profiles obtained by GD-OES (600 Pa, 30 W) in sulphate and chloride baths, respectively (Fernández et al., 2010).

7. Conclusions

Nowadays, a wide variety of complementary analytical tools are available for the compositional, morphological and structural characterization of nanocomposite films. Concerning compositional analysis, the achievement of accurate, precise and sensitive information usually requires of liquid-based samples (e.g. ICP), so the specimen has to be previously dissolved. The need for dissolution steps gives rise to rather lengthy and tedious procedures; moreover, spatial distribution (lateral and depth) is lost. Fortunately, the use of direct solid analysis techniques allows to overcoming the above problem. In particular, the minimal matrix effects typical of GD based techniques allow reliable quantitative depth information with good detection limits and fast analysis times. GDs allow the study of possible processes of diffusion between layers as well as the determination of the nanoparticles concentration and thickness in the coating. Therefore, GD sources have proved to be an excellent analytical tool for the quality control and optimization of the nanocomposite films during which fast chemical in-depth profile information is necessary to ensure their performance.

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Fabrication of High Performance Fe-Si-Al Soft Magnetic Composites

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1. Introduction

Soft magnetic composites (SMC) offers several advantages over traditional soft magnetic materials, for example, new shaping possibilities opens up for 3D design, very low eddy current loss, high magnetic permeability, high resistivity and low coercivity[1]. In recent years, effect of particle size, magnetic particle content, compaction parameters and annealing parameters on properties of soft magnetic composites has been verfied[2-6], and some theoretical works have been studied[7,8]. The conventional Fe-Si-Al (sendust) alloys are known to have several advantages, which include magnetostriction of 0, anisotropy constant of 0, higher electrical resistance, high permeability and lower cost[9,10]. The soft magnetic composites fabricated with Fe-Si-Al powder have a higher performance-cost and have a quick rising output all over the world. But few published information can be found about Fe-Si-Al soft magnetic annealing and dielectric content on properties of Fe-Si-Al soft magnetic powder cores was investigated. Through experimental optimization, the optimum process parameters were obtained.

2. Experimental

The Fe-Si-Al powder containing 85%Fe, 9.6%Si, 5.4%Al was fabricated by water atomization method. The average particle size was about 72µm. The dielectric was mica powder and average particle size was about 26µm. A high temperature silicone adhesive was selected as binder. The powder mixtures of Fe-Si-Al and mica were mixed in bed with spiral mixer with continuous addition of 3.5% silicone adhesive and solution in ethanol solvent. After the evaporation of the solvent, the coated powder was obtained. Following drying, the coated powder was filled into die. Toroidal shape Fe-Si-Al powder cores (outer diameter=27 mm, inner diameter=14.6 mm, high=11.75 mm) were uniaxially cold compacted and kept for 6min. Annealing was carried out at Ar atmosphere for 60 min, and then air cooling. Schematic view of magnetic annealing are shown in Fig.1. Copper bar connetced with power supply of low voltage and DC, and received electric current of 100 A in 15 min. An overview of process parameter and fabricating methods is given in Table 1.

Scanning electron microscopy (SEM) and metallographic microscope (OLYMPUS GX71) were used to characterize the interior structure and morphology of specimens. The

permeability and loss of the Fe-Si-Al powder cores were measured using a B-H analyzer (IWATSU SY-8232).Computer controlled materials tester was used to measure radial crushing strength (RCS) of specimens. The density of specimens was determined by the principle of Archimedes.



Fig. 1. Schematic view of magnetic annealing

Series No.	Shapine pressure (MPa)/annealing temperture (°C) /time/annealing method/dielectric content (wt%)
1	SP/660 °C/1h/annealing/0.7%
	<i>SP</i> =1000,1200,1400,1600,1800,2000.
2	1800/AT/1h/annealing/0.7% 4T=570 590 610 630 640 650 660 680 720
	1800/660 °C/1h/ annealing/0.7%
	1800/660 °C/1h/magnetic annealing/0.7%
3	1800/660 °C/1h/annealing/DC DC=0.4%,0.7%,1.0%,1.3%,1.6%.

SP-shapine pressure, AT-Annealing temperture, DC-dielectric content. Table 1. An overview of process parameters and fabricating methods.

3. Results and discussion

Compaction is an important process in fabricating soft magnetic composites, and the appropriate compaction parameters is a necessary condition to produce high-performance soft magnetic composites. The effect of shaping pressure on density, coercivity, total loss and RCS (radial crushing strength) is given in Fig.2.

We have measured the RCS using equation as following[11]:

$$RCS = P(D-h) / bh^2$$
⁽¹⁾

where D is the outer diameter of sample, h the high of sample, b the thickness of sample and P is crushing load. Fig. 2 shows that density and RCS increase with increasing shaping



Fig. 2. The effect of shaping pressure on density, coercivity, total loss and radial crushing strength (RCS)

pressure. For SMCs spencimens made by powder metallurgy processes, pores were stress concentration centers and higher porosity (lower density) decreased the mechanical strength of specimens. By increasing shaping pressure, the porosity can be decreased and RCS can be improved[4]. Fig.3 shows the metallographic photos of Fe-Si-Al magnetic powder cores in different shaping pressure. It is found that porosity of specimen compacted by 1800 MPa is lower comparing the specimen compacted by 1200 MPa. Fig.2 also shows that total loss and coervicity decrease with increasing shaping pressure. The behavior of coercivity of Fe-Si-Al magnetic powder cores can be explained by following equation[3]:

$$H_{c}(x) = H_{c}(0)[1-x]$$
 (2)

with the coercivity $H_c(0)$ at a magnetic particle content against zero and $H_c(x)$ the coercivity at filler fraction x. It is well known that increasing shaping pressure decreases amount of porosity and further increases x. According to equation (2), the coercivity of Fe-Si-Al magnetic powder cores was decreased by increasing shaping pressure. Generally, the high coercivity can induce the high loss for soft magnetic material[4]. So, total loss and coercivity present similar trend with increasing shaping pressure.



Fig. 3. Shows The metallographic photos of Fe-Si-Al magnetic powder cores in different shaping pressure

Variation of the complex magnetic permeability (μ' and μ'') with frequency in different shaping pressure, for a maximum flux density of 0.07 T, is shown in Fig.4. We can see that up to 50 kHz the real part of permeability does not present a significant decrease. This fact suggests that the limiting frequency for these soft magnetic materials comes up to 50 kHz.



Fig. 4. Variation of the complex magnetic permeability (μ' and μ'') with frequency in different shaping pressure, for a maximum flux density of 0.07 T. ("1000" indicates that powder core was compacted by 1000 MPa)

Seen from Fig.4, the real part of permeability increases with increasing shaping pressure, reaches a peak value, and then decreases. In practice, high permeability can be achieved by high density. But, high density need high pressures[1], and higher pressure would introduce dislocation into the sample, thus create areas that can pin Bloch wall movement[12]. For this series, all samples had the same annealing temperature (660 °C), and the sample compacted by over-1800 MPa did not have a good stress release, and hence domain wall movement was impeded, and the real part permeability fell. So, selecting appropriate shaping pressure is very important to produce high-performance Fe-Si-Al soft magnetic powder cores, and the specimen compacted by 1800 MPa presented the better properties.



Fig. 5. The effect of annealing temperature on loss and effective permeability, for a maximum flux density of 0.07 T, and frequency of 50 kHz.

In series 2, the annealing treatment of Fe-Si-Al magnetic powder cores was researched. In order to produce magnetic powder cores compressed, high pressure should be applied. The internal stresses which have been induced during compaction can deteriorate magnetic properties. Therefore, annealing treatment for reducing internal stresses is essential[6]. Fig. 5 shows the effect of annealing temperature on loss and effective permeability, for maximum flux density of 0.07 T and frequency of 50 kHz. It can be seen that total loss (P_{tot}) and hysteresis loss (P_h) decrease, the eddy current loss (P_e) does not present marked change with increasing annealing temperature. In addition, the effective permeability increases and reaches a maximum of 127 at 660 °C and then decreases with increasing annealing temperature. During compaction, internal stresses are generated in the materials. When the magnetic powder cores were magnetized in AC magnetic fields, the internal stresses impeded domain wall movement, and then led to decrease permeability and increased hysteresis loss and coercivity. The annealing treatment following the compaction can

effectively relieve stresses, and so reduces hysteresis loss and increased permeability. Generally, the higher annealing temperature, the better stress relief, but the overannealing (>660 °C) can degrade the insulation between powder particles and increase amount of porosity, thus increases the presence of eddy currents and decreases permeability. Fig.6 shows SEM image of Fe-Si-Al magnetic powder core at 720 °C annealing. It can be seen that some insulation have been ablated and some voids in interior of Fe-Si-Al magnetic powder core are presented. From above research, increasing annealing temperature can decrease hysteresis loss of Fe-Si-Al magnetic powder cores and increase effective permeability.



Fig. 6. SEM image of Fe-Si-Al magnetic powder core at 720 °C annealing.

Fig.7 shows the variation of effective permeability and total loss with frequency in magnetic annealing and annealing, for a maximum flux density of 0.07T. It is clear that total loss increases with increasing frequency. It is well known that core loss is mainly composited of hysteresis loss and eddy current loss. Hysteresis loss varies linearly with frequency while current eddy loss veries with the square of the frequency[13]. Otherwise, Fig.7 shows that total loss of magentic powder core in magnetic annealing is smaller than that in annealing state, and the effective permeability of two annealing states don't present marked difference. Also, this loss factor in the magnetic annealing state is smaller than that in annealing state. The reasons for reduction in total loss of the sample with magnetic annealing may be explained by improved crystallinity[14]. In the present magnetic field, magnetic domains will be larger and domain growth will be easier[6]. In addition, magnetic moments of atomic pair forming are forced to orient along the magnetic field direction by magnetic annealing, and this behavior also improves the magnetic properties of Fe-Si-Al alloys. The behavior of Fe-Si-Al magnetic powder cores in magnetic annealing haves some difference to H.Shokrollahi's report, which magnetic annealing has influence on the effective permeability [6]. But this behavior of Fe-Si-Al magnetic powder cores is similar to Fe-Si alloys, which magnetic annealing only reduces the loss of Fe-Si alloy[15]. So the addition of Si is a main reason which effective permeability of Fe-Si-Al magnetic powder core with magnetic annealing did not present marked difference comparing annealing.



Fig. 7. Variation of effective permeability and total loss with frequency in magnetic annealing treatment and annealing, for a maximum flux density of 0.07 T.



Fig. 8. The effect of dielectric content on total loss (Ptot), hysteresis loss (Ph) and eddy current loss (Pe), for a maximum flux density of 0.07 T and frequency of 50 kHz.

The core loss of a magnetic device is known to consist of hysteresis loss, eddy current loss. Among these, eddy current loss is dominant in high-frequency range[16]. Eddy current loss comes from two source, the first is eddy current of interior of magnetic powder, which should be reduced by regulating alloy component and inner structure , and another is the eddy current of the interparticle, which should be reduced by coating magnetic powder with dielectric. In fabricating magnetic powder cores, the second method is effective. The effect of dielectric content on total loss, hysteresis loss and eddy current loss is presented in Fig.8. Total loss and eddy current loss decrease with increasing dielectric content. The core with an addition of 0.4% dielectric shows total loss of 89 mW/cm³, and then total loss of core with an addition of 1.6% dielectric decreases to 67 mW/cm³. This can be related to the reduction in eddy current loss is expressed as following:

$$Pe = CB^2 f^2 d^2 / \rho \tag{3}$$

where C is the proportionality constant, B is the flux density, f the frequency, ρ the resistivity and d is the thickness of the material[5]. Decreasing of eddy current loss is due to increasing resistance of Fe-Si-Al magnetic powder cores. Although increasing dielectric content can reduce the loss, it deteriorate permeability. Fig.9 shows that the real part of permeability decreases with increasing dielectric content. It is well known that the real part of permeability strongly depends on the density and magnetic particle content of magnetic powder core, and increasing dielectric content can reduce the density and magnetic particle content. So increasing dielectric content can decrease the real part of permeability.



Fig. 9. Variation of the complex magnetic permeability (μ' and μ'') with frequency in different dielectric content, for a maximum flux density of 0.07 T (" 0.4_DC".indicates that powder core contains 0.4wt% of dielectric content).

In additon, Fig.9 shows that the imaginary part of permeability decreases with increasing dielectric content. As we all know that the imaginary part of permeability reflects the loss of magnetic powder cores, and so the variation of the imaginary part of permeability in Fig.9 accords with the variation of loss in Fig.8. The Fe-Si-Al magnetic powder core with dielectric content of 0.7wt% shows the better magnetic properties.

4. Conclusion

In this paper, the effect of shaping pressure, annealing tempreture, magnetic annealing and dielectric content on properties of Fe-Si-Al soft magnetic composites was investigated. The results showed that increasing shaping pressure can increase density and RCS of Fe-Si-Al soft magnetic cores, and decrease coercivity and total loss. Annealing treatments can eliminate residual stresses and internal defects, and improve the magnetic properties of Fe-Si-Al soft magnetic composites. Increasing annealing temprature can increase effective permeability of specimens and decrease core loss owing to decreasing hysteresis loss. Overannealing (>660 °C) can degrade the insulation between powder particles, and deteriorate magnetic properties. The magnetic annealing can decrease the total loss of Fe-Si-Al magnetic powder cores comparing annealing. Increasing dielectric content can reduce the eddy current loss of Fe-Si-Al magnetic powder core and decrease the real part of permeability.

The Fe-Si-Al magnetic powder core with shaping pressure of 1800MPa, annnealing temperature of 660 °C and dielectic content of 0.7% presents the optimum magnetic properties with an effective permeability of 127, a total loss of 78 mW/cm3 and a radial crushing strength of 18MPa.

5. Acknowledgements

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Spark Plasma Sintered NdFeB-based Nanocomposite Hard Magnets with Enhanced Magnetic Properties

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1. Introduction

Since the discovery of 2:14:1 permanent magnets (PMs) in the early 80's, the nanocrystalline and nanocomposite RE-Fe-B PMs attracted extensive attention both from the academia and industry because of their enhanced magnetic performances and potential applications (Croat et al., 1984; Givord et al., 1984; Hadjipanayis et al., 1984; Onodera et al., 1984; Yamauchi et al., 1985; Jha & Davies, 1989; Pinkerton, 1991; Hadjipanavis, 1999; Liu et al., 2008; Fukagawa et al., 2010). Whereas the enhanced remanence and energy product of nanocrystalline Nd-Fe-B PMs result from the exchange coupling between magnetically hard grains (Manaf et al., 1993), for the nanocomposite PMs the superior magnetic properties are the result of the fine mixture of RE₂Fe₁₄B hard magnetic and Fe-based soft magnetic grains, which are exchange coupled (Kneller & Hawig, 1991). Typically, the exchange coupling in nanophase magnets tends to reduce the coercivity (Mendoza-Suarez et al., 2000) and the energy product decreases with the volume fraction of the magnetic phase, which are well-known challenges in the processing of PMs. The recent work proved the important role played by magnetostatic interactions in the increase of the nucleation and coercive field values of nanocomposite permanent magnets in the detriment of the exchange coupled interactions (Gabay et al., 2006; Marinescu et al., 2008).

The properties of nanocomposite PMs are strongly influenced by a number of process parameters like the composition, preparation method, annealing conditions, distribution of soft and hard magnetic nanograins (Cui et al., 2005). The large values of the remanence are related to the strength of the exchange interactions between the soft and hard magnetic grains, thus the reduction of the grains below the size of the hard magnetic phase domain walls is essential, but they should not decrease below a critical value, dependent on the nanocomposite composition, which causes the reduction of the magnetocrystalline anisotropy of the hard magnetic phase and, consequently, the drastic decrease of the coercive field. Nanocomposite magnets are expected to have maximum energy products as high as 120 MGOe, when the soft and hard magnetic phases are arranged in the proper way and the exchange interactions optimized (Skomski & Coey, 1993). However, the theoretical value of the maximum energy product of NdFeB magnets is calculated to be 512 kJ/m³ (64 MGOe) (Sagawa et al., 1985).

There are two principal manufacturing routes to prepare RE-TM-B nanocomposite PMs: (i) the classical powder metallurgy or sintered magnet process (Sagawa et al., 1984; Durst &

Kronmüller, 1987; Kaneko et al., 2006) and (ii) the rapid solidification or bonded magnet process (McGuiness et al., 1992a; McGuiness et al., 1992b; Tomka et al., 1995; Folks et al., 1995; Zhang & Xiong, 2009). Sintered magnets are prepared from magnetically aligned powders into dense blocks, which are then heat treated, cut to shape, surface treated and magnetized. Bonded magnets are prepared from milled melt-spun ribbons mixed with a polymer or a resin and either compressed or injection moulded. The bonded magnets offer less flux than sintered ones but can be shaped into intricately shaped parts and their eddy current losses are significantly smaller. The melt-spun ribbons can be also hot pressed into fully dense isotropic magnets, and then forged or extruded into high energy anisotropic magnets.

About a decade ago a new technique appeared as an alternative to the conventional sintering methods. Spark Plasma Sintering (SPS) method can consolidate Nd-Fe-B powders at relatively lower temperatures in a short period of time, and the achieved densities of compacted materials can go up to 99% (Liu et al., 1999; Saito, 2001; Ono et al., 2003). But the main and the most important advantage of SPS technique is the high sintering speed, which can effectively hinder the grains growth over the critical nanosize. However, the structure and properties of the compacted materials are dependent on several process parameters, such as the sintering temperature and the applied pressure.

In this following, we will present our results on the preparation and magnetic properties of a few types of Spark Plasma Sintered NdFeB-based nanocomposite magnets prepared from mixtures of ball-milled powders of stoichiometric and non-stoichiometric Nd-Fe-B nanocrystalline melt-spun ribbons and Fe-based amorphous and crystalline materials. The novelty, compared with the already published work on SPS nanocomposite magnets, consists of the use for the first time ever of Fe and Fe-Co- based amorphous/nanocrystalline materials as soft magnetic components.

2. Nd-Fe-B melt spun ribbons

Stoichiometric Nd₁₂Fe₈₂B₆ (Nd12), sub-stoichiometric Nd₈Fe₈₆B₆ (Nd8) and Nd₁₀Fe₈₄B₆ (Nd10), and Nd-rich Nd₁₅Fe₇₉B₆ (Nd15) and Nd₁₆Fe₇₈B₆ (Nd16) master alloys have been prepared by arc melting using a mixture of pure elements in argon atmosphere. The alloys have been re-melted a few times for homogenization and used further to prepare amorphous and nanocrystalline ribbons having thicknesses of 25 µm and widths of 3-5 mm by melt-spinning technique, as shown in Figs. 1 and 2. Whereas the Nd8 XRD pattern (Fig. 1) indicates only the presence of the Fe₃B peak superposed on the broad one of the amorphous phase, the Nd10 ribbon consists of a mixture of α Fe, Fe₃B and amorphous phase. The stoichiometric Nd12 melt-spun ribbons are nanocrystalline in the as-quenched state, but the size of the grains as determined by using the Scherrer formula is around 100 nm, and the presence of the residual amorphous matrix is still present. The DSC curves shown in Fig. 2 indicate also the decrease of the amount of amorphous phase with the increase of the Nd content, and for samples with Nd content over 12 at.% the amorphous phase contribution can not be observed anymore. Whilst the Nd-rich ribbons (Nd₁₅Fe₇₉B₆ and Nd₁₆Fe₇₈B₆) have been further used in the as-quenched state as precursors to prepare powders by high-energy ball-milling, the stoichiometric Nd₁₂Fe₈₂B₆ and sub-stoichiometric Nd₈Fe₈₆B₆ and Nd₁₀Fe₈₄B₆ ones have been first annealed to achieve the optimum nanocrystalline structure and then ball-milled.



Fig. 1. XRD patterns of Nd-Fe-B melt-spun ribbons in the as-quenched state as a function of Nd content.



Fig. 2. DSC curves for Nd-Fe-B melt-spun ribbons vs. Nd content.

The variation of the magnetic characteristics of Nd8, Nd10 and Nd12 melt-spun ribbons as a function of annealing temperature and time are shown in Fig. 3 and Table 1. The coercive field increases with the increase of the Nd content as the result of the increase of the amount of 2:14:1 hard magnetic phase, which in the same time causes a slight decrease of the saturation magnetization and remanence. The coercive field of Nd8 ribbons starts increasing with the annealing temperature, when the 2:14:1 and Fe₃B phases are precipitating. The further increase of the annealing temperature keeps the coercive field almost constant in the temperature range 610-650°C and then starts decreasing slowly due to the increase of the soft magnetic grains. For Nd10 melt-spun ribbons, the presence of α Fe and Fe₃B phases in the as-quenched state results only in the very slight variation of the magnetic characteristics, whereas for the already nanocrystalline Nd12 melt-spun ribbons in the as-quenched state the annealing is refining the nanograins structure and consequently the coercive field increases whereas the saturation magnetization and remanence remain almost unchanged. From Fig. 3 one can conclude that the optimum annealing temperature is 630°C for Nd8 and Nd10 melt-spun ribbons, and 610°C for Nd12 melt-spun ribbons, respectively.



Fig. 3. The variation of the coercive field and remanence as a function of the annealing temperature (T_a) for Nd8, Nd10 and Nd12 melt-spun ribbons.

Keeping the annealing temperature constant we varied the annealing time and the obtained results are given in Table 1.

Composition	Annealing time (min.)	_i H _c (kOe)	$4\pi M_s$ (kG)	$4\pi M_r$ (kG)	M_r/M_s
Nd ₈ Fe ₈₆ B ₆ (T _a =630° C)	10	3.6	13.2	7.6	0.57
	20	4.2	13.1	8.4	0.63
	30	2.8	13.1	7.8	0.60
Nd ₁₀ Fe ₈₄ B ₆ (T _a =630° C)	10	5.0	11.3	8.6	0.75
	20	5.1	11.7	8.4	0.72
	30	5.2	11.0	8.1	0.73
Nd ₁₂ Fe ₈₂ B ₆ (T _a =610° C)	10	5.0	10.8	8.0	0.73
	20	6.2	11.8	8.5	0.74
	30	5.0	10.6	7.6	0.72

Table 1. Magnetic characteristics of Nd-Fe-B melt-spun ribbons vs. annealing time.

The increase of the annealing time from 10 to 20 min. for Nd8 melt-spun ribbons enhances the magnetic characteristics because of the achievement of the full nanocrystalline structure. The further increase of the T_a to 30 min. produces the decoupling of the soft and hard magnetic nanograins due to the increase over the critical size of the soft magnetic nanograins. Due to the already existing nanocrystalline structure in the as-quenched state,

the annealing of the Nd12 melt-spun ribbons at 610°C for 10 min. is enough to refine the nanograins structure and to increase the number of exchange interactions. By increasing even further the annealing time the nanograins are growing excessively and the magnetic properties are altered. The magnetic characteristics of the Nd10 melt-spun ribbons are not changing significantly with the annealing time modification, most probably because of the precipitation in the as-quenched state of soft magnetic α Fe and Fe₃B phases.

3. Nd-Fe-B powders

Nd-Fe-B melt-spun ribbons have been cut in small pieces and then ball-milled in 2 stainless steel vials with 15 stainless steel balls in each vial. It is well known that the characteristics of the sintered magnets are strongly dependent on the magnetic characteristics of the ball-milled powders. The resulting Nd-Fe-B powders have sizes ranging from 20 to 100 μ m. We've noticed that by increasing the milling time the magnetic properties of the powders are deteriorating. This behaviour could have 2 distinct causes: (1) easier oxidation of the powders when they are becoming smaller for longer milling times (despite the fact that milling is done in protective atmosphere), and (2) the precipitation of more Fe-based soft magnetic phase(s) in the detriment of 2:14:1 hard magnetic phase. To minimize the effect of the magnetic characteristics alteration the melt-spun ribbons were milled only for 4 min. Nd-Fe-B powders, and especially those with larger contents of Nd (\geq 12 at.%), are very brittle, so smaller milling times can provide the powders in the desired range of sizes. In Table 2 are presented comparatively the magnetic characteristics for stoichiometric and substoichimoetric Nd-Fe-B melt-spun ribbons and the resulting ball-milled powders with sizes ranging from 20 to 100 μ m.

Composition	Sample type	_i H _c (kG)	$4\pi M_{s}$ (kG)	$4\pi M_r$ (kG)
Nd-For B.	Melt-spun ribbon	4.2	13.2	8.4
INU8Fe86D6	Powders	4.3	12.0	7.3
Nd ₁₀ Fe ₈₄ B	Melt-spun ribbon	5.0	11.9	8.9
	Powders	5.2	11.0	7.5
Nd ₁₂ Fe ₈₂ B ₆	Melt-spun ribbon	6.3	11.2	8.4
	Powders	7.7	10.3	6.6

Table 2. Magnetic characteristics for annealed melt-spun ribbons and the resulting powders.

One can notice the increase of the coercive field and the slight decrease of the saturation magnetization and remanence for the resulting powders. The increase of the coercive field is more pronounced for the powders with larger Nd contents, most probably as a result of the decoupling between the soft and hard magnetic phases, as shown in Fig. 4. For Nd8 and Nd10 powders the exchange coupling is improved (the shoulder in the second quadrant disappears) compared with the precursor melt-spun ribbons, confirming the previously observed results for milled powders used to make bonded magnets (McGuiness et al., 1992a; McGuiness et al., 1992b; Tomka et al., 1995; Folks et al., 1995; Zhang & Xiong, 2009). A consequence of better exchange coupling between the soft and hard magnetic grains is also the small reduction of the remanence for Nd8 and Nd10 ball-milled powders. It is important to note also that the magnetization hysteresis loop for Nd12 powders is not saturated, but clearly shows the presence of 3 magnetic phases: soft magnetic α Fe and Fe₃B and hard magnetic 2:14:1 phase, whereas the melt-spun ribbons consist only of α Fe soft magnetic and 2:14:1 hard magnetic phase.



Fig. 4. Magnetic hysteresis curves for Nd10 and Nd12 annealed melt-spun ribbons (at 630°C for 20 min. for Nd10 and 610°C for 10 min. for Nd12), respectively, and the resulting ball-milled powders with sizes ranging from 20 to 100 μ m.

Fig. 5 presents the hysteresis loops for $Nd_{15}Fe_{79}B_6$ melt-spun and ball-milled powders of 63-80 μ m as well as for $Nd_{16}Fe_{78}B_6$ melt-spun and powders in the range size of 80-100 μ m.



Fig. 5. Magnetic hysteresis curves for Nd15 and Nd16 as-quenched melt-spun ribbons and the resulting ball-milled powders with sizes ranging from 63 to $100 \,\mu$ m.

As one can see the hysteresis curves of powders are constricted compared with the meltspun ribbon's ones, which might be an indication that during ball-milling the precipitation of more Fe-based phases is favoured in the detriment of 2:14:1 phase and the decoupling is more evident. Additionally, the magnetic behaviour of Nd-rich alloys powders is strongly dependent on the powders size compared with the stoichiometric and sub-stoichiometric compositions for which we didn't notice such a behaviour. The optimum magnetic properties are achieved for Nd15 powders in the 63-80 μ m range and respectively for Nd16 powders with sizes between 80 and 100 μ m, as shown in Fig. 6. Most probably, this behaviour is a collective process which involves both the surface oxidation effects (despite the fact that the ball-milling is done in protective Ar atmosphere) and the grains size refinement. It is worthwhile to note the high values of the coercive field obtained for both Nd15 and Nd 16 melt-spun nanocrystalline ribbons and ball-milled powders of about or over 20 kOe, but also the moderate values of the remanence which are a clear proof that the predominant phase is 2:14:1, whereas the volume of Fe-based soft magnetic phases is much smaller compared with Nd8, Nd10 and Nd12 samples. One should also notice that the applied field of 3 T used in this work is not enough to saturate either the melt-spun ribbons or ball-milled powders.



Fig. 6. Demagnetization curves for Nd15 and Nd16 ball-milled powders in the size range 10- $150 \mu m$.

4. Soft magnetic materials used as precursors for SPS nanocomposite PMs

For this study we have chosen a number of soft magnetic materials to be used as precursor for preparing SPS nanocomposite magnets: (1) $Fe_{77.5}Si_{7.5}B_{15}$ (FeSiB) (4 π M_s ~ 16 kG) and (2) $Co_{68,25}Fe_{4,5}Si_{12,25}B_{15}$ (CoFeSiB) (4 π M_s ~ 8 kG) conventional amorphous wires (CAW) of 100-125 µm in diameter prepared by in-rotating water quenching method (Ohnaka, 1985; Vazquez & Chen, 1995; Chiriac et al., 1998); (2) Co_{68.2}Fe_{4.45}Mn_{0.1}Si_{12.25}B₁₅ (CoFeMnSiB) amorphous melt-spun ribbons ($4\pi M_s \sim 8 \text{ kG}$) (Hilzinger & Kunz, 1980; Makino et al., 1990; Chiriac et al., 1997); (3) Fe_{73.5}Nb₃CuSi_{13.5}B₉ (FINEMET) nanocrystalline melt-spun ribbons $(4\pi M_s \sim 12.4 \text{ kG})$ (Yoshizawa et al., 1988); (4) Fe₂Co crystalline melt-spun ribbons $(4\pi M_s \sim 22)$ kG); and (5) commercial Fe micropowders ($4\pi M_s \sim 20$ kG) of about 10 μ m. The studies done up to know on Nd-Fe-B nanocomposite bulk magnets (sintered or bonded) used either Fe (Wei et al., 1994; McCormick et al., 1998; Lewis et al., 2001; Rada et al., 2005; Niu et al., 2007; Bhame et al., 2010; Cha et al., 2010) or Fe₂Co micro or nanopowders (Wei et al., 1994) to increase the remanence and saturation magnetization of the respective PMs, whereas Fe, Fe-Co and Fe-B have been used in combination with Nd-Fe-B to prepare multilayered structures by deposition methods (Shindo et al., 1996; Cui & O'Shea, 2004; Ao et al., 2005; Kato et al., 2005). Additionally, other attempts to prepare nanocomposite PMs used combinations of Nd-Fe-B and Sm-Co-based particles (Talijan, 2006; Betancourt & Davies, 2010). However, excepting the multilayered structures obtained by deposition, most of the other studies are related to nanocomposite magnets prepared by milling of the starting Nd-Fe-B alloys followed by mixing with Fe-based soft magnetic materials and then annealing of the full composite, and not by milling the melt-spun ribbons in the as-quenched state or after annealing. Our goal is to use soft magnetic high saturation magnetization materials in combination with Nd-Fe-B ball milled powders.

FeSiB and CoFeSiB CAW have been cut in small pieces and then ball-milled in argon atmosphere for 6 h. The resulting micropowders have sizes between 5 and 150 μ m, and their magnetic properties are almost independent of the powders size (Fig. 7) compared with Nd-Fe-B ball milled powders. The amorphous state is preserved even after milling for 6 h, as shown by the structural studies.



Fig. 7. Magnetic hysteresis curves for FeSiB and CoFeSiB as-quenched conventional amorphous wires (CAW) and the resulting ball-milled powders.

The same behaviour was observed for amorphous CoFeMnSiB and FINEMET powders prepared from amorphous and respectively nanocrystalline melt-spun ribbon precursors. The amorphous FINEMET ribbons have been annealed at 560°C for 1 h to achieve the optimum α Fe nanograins size (~ 10 nm) and then ball-milled for 20 h. The same milling time was used to prepare powders from CoFeMnSiB amorphous ribbons. After milling the nanocrystalline structure of FINEMET ribbons and respectively the amorphous structure of CoFeMnSiB melt-spun ribbons are preserved, and the ball-milled powders show almost identical XRD patterns.

X-ray diffraction pattern of Fe₂Co (FeCo) melt-spun ribbons of 25 μ m thick prepared by melt-spinning reveals only the bcc lines. The same structure is preserved after ball-milling the ribbons for 24 h. The magnetic characteristics measured for the precursor melt-spun ribbons and ball-milled powders are almost similar, with saturation magnetization of about 22 kG.

The commercial Fe micropowders of 10 μ m used in this study to prepare SPS nanocomposite magnets have a saturation magnetization of ~20 kGs, a little bit lower than the saturation magnetization of bulk Fe (~ 22 kG), indicating the presence of some traces of Fe oxides on their surface as confirmed by XRD measurements (very small peaks corresponding to Fe₂O₃ can be identified along with the bcc lines of Fe).

5. Spark Plasma Sintered (SPS) nanocomposite magnets

Nd-Fe-B and soft magnetic materials powders have been mixed in different ratios (80:20; 90:10; 92:8; 94:6; 95:5 and 96:4, respectively), placed into a carbon die, and then sintered under vacuum by SPS. The temperature of the specimen was increased from room

temperature to the consolidating temperature of 600°C for 300 s and then held at the consolidating temperature for 300 s by applying a pulsed electric current of 800 A at intervals of 2.4 ms. The temperature was measured using a thermocouple placed on the surface of the sample. The specimens have been prepared at different pressures ranging from 50 to 80 MPa, applied during the heating. After the SPS consolidation, the samples have been cooled down to room temperature without applying pressure. The specimens were 10 mm in diameter and 2-5 mm in thickness. Their structural and magnetic properties have been investigated afterwards by means of X-ray diffractometry (BRUKER AXS D8-ADVANCE XRD), scanning electron microscopy combined with EDS (Carl Zeiss CrossBeam Neon 40 EsB), and vibrating sample magnetometry (LakeShore 7410 VSM).

Fig. 8 shows the XRD patterns for a number of Nd-Fe-B/soft magnetic material SPS nanocomposite magnets. One can notice that after spark plasma sintering the 2:14:1 phase is preserved and additional peaks corresponding to α Fe(Co) and Fe₃B soft magnetic phases can be easily identified. However, the amount of soft magnetic phases is larger compared with the Nd-Fe-B melt-spun precursors due to the supplementary addition of Fe and Co-Fe based soft magnetic materials. As smaller the amount of Nd in the precursor Nd-Fe-B powders, as larger the amount of 2:14:1 phase is, contrary to the expectations. This means the addition of soft magnetic powders is contributing to the precipitation of a larger amount of 2:14:1 phase in the nanocomposite samples.



Fig. 8. XRD patterns of Nd-Fe-B/soft magnetic powders SPS nanocomposite magnets.

The formation of a larger amount of 2:14:1 hard magnetic phase is also demonstrated by the thermomagnetic curves presented in Fig. 9. It is worth noticing that the largest saturation magnetization is achieved for Nd12-4FeCo SPS nanocomposites and also a significant increase is observed for all Nd-Fe-B/FeCo nanocomposite samples as expected. The presence of α Fe is observed for all nanocomposite samples ($T_C \sim 770^\circ$ C) and the largest amount of soft magnetic α Fe is present in Nd-Fe-B/Fe magnets.



Fig. 9. M-T curves for Nd-Fe-B/soft magnetic powders SPS nanocomposite magnets. The thermomagnetic curves for Nd15 and Nd16 melt-spun ribbons are shown for comparison.

The values of the magnetic characteristics for several Nd-Fe-B/FeSiB and Nd-Fe-B/CoFeSiB nanocomposite magnets prepared by SPS are shown in Table 3.

Sample	$4\pi M_r$ (kG)	_i H _c (kOe)	(BH) _{max} (MGOe)			
Nd ₁₅ Fe ₇₉ B ₆						
Melt-spun ribbons	5.0	20.30	6.2 (25.4)			
Ball-milled powders (63-80 μm)	6.3	19.01	9.9 (29.9)			
NdFeB-4FeSiB / 70 MPa	5.8	16.02	8.4 (23.2)			
NdFeB-5FeSiB / 50 MPa	6.5	17.85	10.6 (29.0)			
NdFeB-10FeSiB / 50 MPa	5.9	16.97	8.7 (25.0)			
NdFeB-5CoFeSiB / 50 MPa	6.2	17.45	9.6 (27.0)			
NdFeB-10CoFeSiB / 50 MPa	5.4	15.13	7.3 (20.4)			
Nd ₁₆ Fe ₇₈ B ₆						
Melt-spun ribbons	4.82	20.44	5.8 (24.6)			
Ball-milled powders (80-100 μm)	5.70	16.17	8.1 (23.0)			
NdFeB-4FeSiB / 50 MPa	6.27	17.41	9.9 (27.3)			
NdFeB-5FeSiB / 50 MPa	5.87	16.97	8.7 (24.9)			
NdFeB-4CoFeSiB / 50 MPa	6.11	17.41	9.3 (26.6)			
NdFeB-5CoFeSiB / 50 MPa	5.99	17.02	9.0 (25.5)			

Table 3. The magnetic characteristics of several Nd-Fe-B/FeSiB and Nd-Fe-B/CoFeSiB nanocomposite magnets prepared by SPS method, as a function of the hard to soft materials ratio and the applied pressure during consolidation. The $(BH)_{max}$ values in the brackets are calculated for a packing degree of 98% (Lupu et al., 2009) and for an applied field of 50 kOe.

The largest coercive field is obtained for melt-spun ribbons, whilst the powders show larger values of the remanence. By consolidation through the SPS technique the maximum energy product generally increases for optimal processing parameters, the highest increase of about 10% being obtained for Nd16-4FeSiB nanocomposite magnet consolidated at 50 MPa. The degree of compaction for the below mentioned samples is reaching 65%, and if we extrapolate the data to an apparent density of 98% (Saito et al., 2004) and we assume the

samples are saturated in an external field of 50 kOe then the maximum energy product for our isotropic SPS nanocomposite magnets is reaching values of 25-29 MGOe, comparable with those obtained up to now for anisotropic nanocomposite magnets (Saito, 2001; Yue at al., 2003).

Fig. 10(a) presents comparatively the dM/dH=f(H) curves for Nd15 ball-milled powders and 2 SPS nanocomposite magnets (Nd15-5FeSiB and Nd15-5CoFeSiB), both consolidated at 50 MPa, whilst Fig. 10(b) shows the variation of dM/dH with the soft magnetic material content for the same consolidating pressure.



Fig. 10. dM/dH=f(H) curves for Nd15 ball-milled powders and SPS consolidated nanocomposite magnets as a function of added soft magnetic material (Lupu et al., 2009).

One can notice that despite the fact that the powders exhibit larger coercive field, the coupling between the soft and hard magnetic phases is improved for nanocomposite magnets. The strength of the decoupling is indicated by the second shoulder of dM/dH=f(H) curves located nearby Y axis, which is very small for SPS consolidated nanocomposite magnets, but also by the height of the first peak. In this case, it is hard to believe that only the intergranular exchange coupling is responsible for such behaviour, but most probably a collective process of both exchange and magnetostatic interactions between the powders of the 2 materials forming the nanocomposite (Gabay et al., 2006).

The same behavior is observed for Nd16 powders and nanocomposite magnets, as indicated in Fig. 11. As expected, the exchange coupling plays the predominant role in melt-spun nanocrystalline ribbons and the presence of the second shoulder is missing, whereas for the composites the magnetostatic interactions becomes more predominant (see also Fig. 12). However, the percentage of exchange interactions contribution to the macroscopic response of the nanocomposite systems is still very important, considering that usually the magnetostatic interactions are reducing the coercive field values.

The maximum energy product increases with about 13% for Nd15/soft magnetic material and Nd16/soft magnetic material nanocomposite SPS magnets. The optimum sintering temperature is 50 MPa.

The interactions between the nanograins of SPS nanocomposite magnets were examined by using the δM plot, defined as:

$$\delta M(H) = m_d(H) - [1 - 2m_r(H)],$$

where m_d is the reduced demagnetization remanence and m_r is the reduced isothermal remanence. According to Wohlfarth's model (Wohlfarth, 1958), a positive δM peak indicates an exchange coupling process, while a negative δM peak indicates magnetostatic interactions between the magnetically hard and soft phases. A sharp peak indicates strong exchange interactions between the constituent grains, and a less pronounced peak reveals weak exchange intergranular interactions.



Fig. 11. dM/dH=f(H) curves for Nd16 melt-spun ribbons, ball-milled powders and SPS consolidated nanocomposite magnets as a function of added soft magnetic material (Lupu et al., 2009).



Fig. 12. Magnetic hysteresis loops for Nd-Fe-B nanocomposite SPS magnets. The M-H loops for Nd15 and Nd16 melt-spun ribbons and precursor ball-milled powders are also plotted for comparison.

In Fig. 13 are presented the δM curves for Nd15/FeSiB and Nd15/CoFeSiB SPS nanocomposites with different contents of soft magnetic material. The magnets with less soft magnetic component show larger δM values, i.e. stronger exchange interactions between the nanograins, confirming the large values of the remanence and maximum energy product presented in Table 3.



Fig. 13. δ M curves for Nd₁₅Fe₇₉B₆/FeSiB and Nd₁₅Fe₇₉B₆/CoFeSiB SPS nanocomposite magnets as a function of the soft magnetic component content. Powders with sizes ranging from 63 to 80 µm were used to prepare the magnets and a pressure of 50 MPa was applied during SPS process.

The sintering pressure not only displaces the powders to fill the empty spaces but introduces also some frictions between particles. The generated heat during the filling of the empty volume as well as the heat generated through Joule effect when the electrical current is passing through the sample and the local discharges between particles will melt superficially the particles external surface, but due to the very short time of pressing and passing the current through the powders mixture the melt will solidify rapidly and will assure a very strong bonding between the particles. In this way, large density nanocomposite magnets are produced.

Table 4 presents the magnetic characteristics of nanocrystalline FINEMET and amorphous CoFeMnSiB melt-spun ribbons as well as for the Nd-Fe-B/FINEMET and Nd-Fe-B/CoFeMnSiB SPS nanocomposite magnets. The magnetic properties of the SPS magnets are altered slightly compared with the Nd16 precursor powders due most probably by the mechanical deformations induced during SPS processing. Once the amount of FINEMET powders is increasing, the saturation magnetization increases because of the higher saturation value of FINEMET compared with Nd16 powders, whilst when increasing the CoFeMnSiB content the situation is opposite due to the lower saturation magnetization of Co-based amorphous alloy. However, the largest values for the coercive field and the maximum energy product are obtained for Nd16/CoFeMnSiB SPS magnets, as a consequence of the stronger exchange interactions between the nanograins of the soft amd hard magnetic phases. For both types of SPS nanocomposite magnets the optimum magnetic properties are obtained for a sintering pressure of 60 MPa.

The coercive field is determined by two main factors: (1) the pinning of the domain walls and (2) the nucleation of the reversed magnetic domains. The simultaneous presence of the two mechanisms is confirmed by the shape of the first magnetization curve for Nd16/FINEMET SPS magnets prepared at two different sintering pressures and shown in Fig. 14. For the SPS magnets sintered at 50 MPa the coercive field is mainly determined by the nucleation mechanism, whereas for the larger sintering pressure of 60 MPa the pinning mechanism becomes predominant.

Sample	_i H _c (kOe)	4πM _{3T} (kG)	$4\pi M_r$ (kG)	(BH) _{max} (MGOe)
FINEMET ribbons	1.5x10-3	12.2	9.5	
CoFeSiBMn ribbons	5.0x10 ⁻³	6.7	5.2	
Nd ₁₆ Fe ₇₈ B ₆ ribbons	20.0	8.9	6.9	11.9
NdFeB-4FINEMET / 50MPa	18.0	9.0	6.0	9.0
NdFeB-4FINEMET / 60MPa	18.5	9.0	6.3	9.9
NdFeB-5FINEMET / 50MPa	17.7	9.1	6.2	9.6
NdFeB-5FINEMET / 60MPa	18.0	9.1	6.3	9.9
NdFeB-6FINEMET / 50MPa	18.5	9.2	6.0	9.0
NdFeB-6FINEMET / 60MPa	18.0	9.2	5.9	8.7
NdFeB-4CoFeMnSiB / 50MPa	17.2	8.7	6.0	9.0
NdFeB-4CoFeMnSiB / 60MPa	19.5	8.4	6.1	9.3
NdFeB-5CoFeMnSiB / 50MPa	16.8	8.5	5.9	8.7
NdFeB-5CoFeMnSiB / 60MPa	18.2	8.8	6.4	10.2
NdFeB-6CoFeMnSiB / 50MPa	19.5	8.7	6.2	9.6
NdFeB-6CoFeMnSiB / 60MPa	17.7	8.7	6.3	9.9

Table 4. Magnetic characteristics for nanocrystalline FINEMET and Nd16 ribbons, CoFeMnSiB amorphous ribbons as well as for SPS nanocomposite magnets prepared by combining the Nd16 hard magnetic and FINEMET or Co-based soft magnetic powders.



Fig. 14. The first magnetization curves for Nd16-6%FINEMET SPS magnets sintered at 2 different sintering pressures.

In Fig. 15 are presented comparatively the hysteresis loops for Nd16/FINEMET and Nd16/CoFeMnSiB SPS nanocomposite magnets sintered at the same sintering pressure (60 MPa). The remanence and coercive field for the 2 nanocomposite magnets are almost the same, but the presence of the shoulder in the second quadrant is almost not visible for the Nd16/CoFeMnSiB magnets because of the better exchange coupling of the soft and hard magnetic phases.

Fig. 16 shows the backscattered SEM micrographs of Nd16/5Fe SPS magnets consolidated at two pressures: 50 MPa (a) and 80 MPa (b). One can notice the difference in the morphologies of the two magnets and the fact that higher pressures are melting the powders

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Fig. 15. Magnetic hysteris loops for Nd16/FINEMET and Nd16/CoFeMnSiB SPS nanocomposite magnets sintered at 60 MPa.

boundaries and the resulting material is similar with a bulk one. Both magnets prepared at 50 and 80 MPa, respectively, are mainly consisting of primary Nd₂Fe₁₄B hard magnetic phase and secondary aFe soft magnetic phase, as proved by XRD patterns shown in Fig. 8.



Fig. 16. BSE-SEM micrographs of Nd16Fe78B6+5 wt.% Fe SPS magnets consolidated at: (a) 50 MPa and (b) 80 MPa.

The magnetic characteristics of Nd-Fe-B/Fe SPS nanocomposite magnets are shown in Table 5. The remanence increases from 6.4 kG for Nd15 SPS magnets without addition of Fe to 6.6 kG for Nd15/5 wt.% Fe SPS magnets consolidated at the same pressure of 50 MPa. Further increase of Fe powders content leads to the decrease of the remanence to 5.6 kG for Nd15/10 wt.% Fe SPS magnets consolidated at 50 MPa. The enhancement of the remanence of the SPS nanocomposite magnets comes from the exchange interactions between the powders of the hard and soft magnetic phases, respectively. The increase of the Fe powders content leads to a slight decrease of the coercivity, too. A more evident proof of the increasing role of exchange interactions in SPS nanocomposite magnets appears when comparing the melt-spun ribbons, the precursor powders and the SPS samples. Whereas in the ribbons the coupling between the grains of the hard and soft magnetic phases is very good, it is deteriorating for the powders and the decoupling shoulder appears on the M-H loops. The decoupling is becoming less evident for SPS nanocomposite magnets with 4 and 5 wt.% Fe, and is reappearing for larger contents of Fe powders. The coercive field also increases with the Fe powders content to 5 wt.%, reaching almost the value obtained for melt-spun ribbons

in the as-quenched state. A similar behaviour is observed for Nd16 SPS consolidated magnets. The magnetic properties are altered for all SPS nanocomposite magnets consolidated at higher pressures (80 MPa). Correlating the microstructure evolution with the observed changes in their magnetic properties, the alteration could be determined by the effect of both the distance modification between particles and their deformation (see Fig. 16, too). By consolidation through the SPS technique the maximum energy product generally increases for optimal processing parameters, the highest increase of about 8 % being obtained for Nd15/5 wt.% Fe SPS nanocomposite magnets consolidated at 50 MPa compared with the similar Nd15 SPS magnets prepared in the same conditions.

Sample	_i H _c (kOe)	$4\pi M_r$ (kG)	(BH) _{30G} (MGOe)			
Nd ₁₅ Fe ₇₉ B ₆						
Nd15 / 50MPa	17.8	6.4	10.2			
Nd15-4Fe / 50MPa	17.4	6.6	10.9			
Nd15-4Fe / 80MPa	17.2	6.4	10.2			
Nd15-5Fe / 50MPa	18.1	6.6	10.9			
Nd15-5Fe / 80MPa	17.2	6.5	10.6			
Nd15-10Fe / 50MPa	16.8	6.0	9.0			
Nd15-10Fe / 80MPa	15.8	5.6	7.8			
Nd ₁₆ Fe ₇₈ B ₆						
Nd16 / 50MPa	17.5	6.1	9.3			
Nd16-4Fe / 50MPa	17.4	6.4	10.2			
Nd16-4Fe / 80MPa	16.7	6.2	9.6			
Nd16-5Fe / 50MPa	16.7	6.4	10.2			
Nd16-5Fe / 80MPa	16.5	5.9	8.7			
Nd16-10Fe / 50MPa	15.5	6.2	9.6			
Nd16-10Fe / 80MPa	15.0	5.9	8.7			

Table 5. Magnetic characteristics for Nd15, Nd16, Nd15/Fe and Nd16/Fe SPS nanocomposite magnets.

Fig. 17 presents comparatively the δM curves for Nd15/Fe SPS nanocomposite magnets consolidated at 50 MPa. When the applied field is small and the nanocomposite magnet is in the initial magnetization state the magnetic moments within the nanograins are randomly oriented and the distribution of angles between adjacent moments is broad. Hence, there are exchange interactions between nanograins and δM has positive values (the ascending part of the δM plots). The increase of the applied field favors the alingnment of the neighboring magnetic moments in the nanograins and the exchange interactions become predominant. Consequently, δM increases and reaches a peak. The shift of the maximum field value to larger fields for 4 wt.% Fe and 5 wt.% SPS nanocomposite magnets is also consistent with the increase in coercivity (Table 5). Additionally, a higher δM peak indicates stronger exchange interactions between the nanograins of the magnetically hard and soft phases. The strongest exchange interactions are observed for a content of 5 wt. % Fe. While the applied field approaches the coercivity (Fig. 17 and Table 5), the moments basically cancel out each other and the effective magnetization in the direction of applied field approximates to zero. Thus, the magnetostatic interactions are still very weak and the exchange interactions are

predominant giving positive δM values. With the continuous increase of the applied field the magnetic moments are gradually aligned parallel in each grain and the dipolar interactions between nanograins are becoming more important compared with the exchange interactions. Consequently, δM becomes slightly negative.



Fig. 17. δ M plots for Nd15/Fe SPS nanocomposite magnets consolidated at 50 MPa.

M-H loops for Nd16/FeCo SPS nanocomposite magnets presented in Fig. 18 show that the largest coercive field is reached for 96Nd16:4FeCo. For this ratio the exchange coupling is the strongest and no decoupling is visible in the second quadrant. By increasing the FeCo content the decoupling between soft and hard magnetic nanograins is evident and the shoulder appearing on the demagnetization curves is more pronounced.



Fig. 18. Magnetic hysteris loops for Nd16/FeCo SPS nanocomposite magnets sintered at 50 MPa. The hystersis loop for the precursor Nd16 powders is shown for comparison.

Whereas the coercive field values are increasing with the increase of Nd content in the hard magnetic phase precursors, the largest values of the maximum energy product are achieved for Nd12/4FeCo SPS nanocomposite magnets (Table 6).

Sample	Hc (kOe)	$4\pi M_s$ (kG)	$4\pi M_r$ (kG)	(BH) _{max} (MGOe)
Nd8-4FeCo	4.0	10.8	5.7	8.1
Nd8-10FeCo	3.6	13.3	7.1	12.6
Nd10-4FeCo	5.2	10.1	6.2	9.6
Nd10-10FeCo	4.7	12.8	7.2	12.9
Nd12-4FeCo	10.0	10.4	7.6	14.4
Nd12-10FeCo	8.4	11.5	6.6	10.9
Nd15-4FeCo	13.0	9.1	6.5	10.5
Nd15-10FeCo	12.0	9.6	5.5	7.6
Nd16-4FeCo	17.6	8.4	5.8	8.4
Nd16-10FeCo	13.9	9.0	5.7	8.1

Table 6. The magnetic characteristics of Nd-Fe-B/FeCo SPS nanocomposite magnets sintered at 50 MPa.



Fig. 19. $\delta M(H)$ curves as a function of Nd content in the hard magnetic component precursors. All SPS nanocomposites magnets contain the same amount of Fe₂Co powders, i.e. 4 wt.%, and they are consolidated at 50 MPa.

For nanocomposite magnets with low contents of Nd (Nd8/4FeCo and Nd10/4FeCo) the values of δM shown in Fig. 19 are negative suggesting that the interactions between the soft and hard magnetic nanograins have dipolar (long-range magnetostatic) character and promote the demagnetized state. The magnetostatic interactions reduce the number of irreversible magnetization processes during magnetization in comparison with those occurring during demagnetization. The positive δM curves for Nd-rich (Nd15/4FeCo and Nd16-4FeCo) nanocomposite magnets suggest stronger exchange interactions dominating the magnetization processes. δM increases for Nd12/4FeCo nanocomposite magnets and exhibits a peak on the positive side when increasing the applied field, then decreases to zero and changes to negative for much larger applied fields than the coercive field (Fig. 19 and Table 6).

The highest positive peak is obtained for Nd15/4FeCo nanocomposite magnets, suggesting predominant exchange interactions in the detriment of the magnetostatic ones. The same

behaviour is observed independent of the FeCo content in the Nd-Fe-B/FeCo SPS nanocomposite magnets.

Fig. 20 presents the first magnetization curves for Nd8/4FeCo, Nd10/4FeCo and Nd12/4FeCo SPS nanocomposite magnets sintered at 50 MPa.



Fig. 20. First magnetization curves for NdFeB/FeCo SPS nanocomposite magnets consolidated at 50 MPa.

From the shape of the first magnetization curves we can conclude that for Nd8/4FeCo and Nd10/4FeCo magnets the nucleation of the domain walls with reversed magnetization is predominant, whereas the mechanism is changed to the domain wall pinning for Nd12/4FeCo. This is related also to the fact that in Nd12/4FeCo nanocomposite magnets the amount of 2:14:1 phase is larger than for the sub-stoichiometric (Nd 8 and Nd10) compositions or Nd-rich compositions (Nd 15 and Nd16). The increase of the sintering temperature from 600°C to 650°C or of the sintering time from 5 to 7 min. results in the deterioration of the magnetic properties due to the increased amount of soft magnetic phases as well as to the increase of the nanograins size from 20-30 nm to 150-200 nm. A temperature below 600°C or a sintering time shorter than 5 min. are not enough for a good bonding between the hard and soft magnetic components, even at a higher sintering pressure of 80 MPa. The increase of the sintering pressure from 50 to 80 MPa increases a little bit the remanence, but leaves the coercive field almost constant.

6. Conclusions and future perspectives

Nanocomposite permanent magnets have been obtained by SPS consolidation of powders of different hard and soft magnetic materials in different ratios. The powders have been obtained by ball-milling the NdFeB hard magnetic nanocrystalline melt-spun ribbons precursors and respectively FeSiB or CoFeSiB amorphous wires, FINEMET nanocrystalline melt-spun ribbons, CoFeMnSiB amorphous melt-spun ribbons, Fe₂Co fully crystalline melt-spun ribbons or Fe commercial micropowders.

Despite the fact that the powders exhibit larger coercive fields, the coupling between the soft and hard magnetic phases is improved for nanocomposite magnets. The strength of the decoupling is indicated by the second shoulder of dM/dH=f(H) curves located nearby Y

axis, which is very small for SPS consolidated nanocomposite magnets. Most probably a collective process of both exchange and magnetostatic interactions between the powders of the 2 materials forming the nanocomposite is responsible for such specific behaviour. The exchange coupling plays the predominant role in Nd-Fe-B melt-spun nanocrystalline ribbons, whereas the magnetostatic interactions becomes more predominant for Nd-rich nanocomposites. However, the percentage of exchange interactions contribution to the macroscopic response of the nanocomposite systems is still very important, considering that usually the magnetostatic interactions are reducing the coercive field values.

The magnetic properties can be tailored by choosing the proper SPS consolidation conditions and the optimum ratios of the 2 or more different phases forming the nanocomposites.

Further studies on increasing the amount of soft magnetic component and the sintering pressure are necessary to increase the maximum energy product and to reach at least the values obtained for existing sintered magnets (maximum 55 MGOe), if not the calculated ones (64 MGOe) (Sagawa et al., 1985). To achieve this goal, the preparation of anisotropic SPS nanocomposite magnets consisting of Nd-Fe-B hard magnetic and Fe or Co-Fe based soft magnetic materials is imperiously necessary. Another goal is to increase the operating temperature of these magnets from 100-150°C to at least 250-300°C by adding to the Nd-Fe-B hard magnetic component Co-based materials or other additives which could increase the Curie temperature of these SPS nanocomposite PMs.

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Advanced Anticorrosive Coatings Prepared from Polymer-Clay Nanocomposite Materials

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1. Introduction

Corrosion control is an important subject of increasing interest to the modern metallic finishing industry. Surface modification of metallic substrates by organic or polymeric coatings is an essential approach for enhancing surface properties such as wear, oxidation, and corrosion. Various conventional techniques are utilized to depositing the desired materials onto the metallic substrate to achieve surface modifications with better protection for the substrate. Organic or polymeric coatings on metallic substrates provide an effective barrier between the metal and its environment and/or inhibit corrosion through the presence of chemicals. Chromium-containing compounds (CC) have generally been used as effective anticorrosive coatings in the past decades. However, due to the environmental and health concerns, CCs may need to be replaced by alternative materials that would not pose biological and ecological hazards. Thus, research has focused on the development of novel polymeric coating materials that contain effective anticorrosive agents.

During the early stage of corrosion protection engineering, various neat organic or polymeric coatings were developed. These coatings generally function as a physical barrier against aggressive species such as O_2 and H⁺ that cause decomposition. Examples of representative polymers are include epoxy resins [MacQueen & Granata, 1996; Dang et al., 2002], polyurethanes [Moijca et al., 2001], and polyesters [Malshe & Sangaj, 2006; Deflorian et al., 1996]. Moreover, conjugated polymers such as polyaniline [Wessling & Posdorfer, 1999; Tan & Blackwood, 2003], polypyrrole [Iroh & Su, 2000, Krstajic et al., 1997], and polythiophene [Kousik et al., 2001], have also been employed as advanced anticorrosive coatings due to their redox catalytic properties, forming metal oxide passivation layers on metallic substrates. Conversely, not all neat polymeric coatings are permanently impenetrable because small defects in the coatings can lead to gateways that allow corrosive species to attack the metallic substrate; thus, localized corrosion can occur. As a second line of defense against corrosion, various nanoscale inorganic additives have been incorporated into various polymer matrices to generate a series of organic-inorganic hybrid anticorrosive coatings.

Recently, montmorrillonite (MMT)-layered silicate (clay) has attracted intensive research interest for the preparation of polymer-clay nanocomposites (PCNs) because its lamellar elements display high in-plane strength, stiffness, and high aspect ratios. Typically, the chemical structures of MMT consist of two fused silica tetrahedral sheets that sandwich an

edge-shared octahedral sheet of either magnesium or aluminum hydroxide. The Na⁺ and Ca⁺² residing in the interlayer regions can be replaced by organic cations such as alkylammonium ions, by a cationic-exchange reaction to render the hydrophilic clay organophilic. The historical development of polymer-clay nanocomposites can be traced back to the work of PCNs reported by Toyota's research group [Usuki et al., 1993]. According to many recently published works, the dispersion of clay was found to boost the thermal stability [Lan et al., 1994], mechanical strength [Tyan et al., 1942], and molecular-barrier [Wang & Pinnavaia, 1998] and flame-retardant [Gilman et al., 2000] properties of polymers. Recently, we reported that the dispersion of MMT platelets into various polymeric materials, in the form of coatings, boosted the corrosion protection of the polymer on metallic electrodes based on a series of electrochemical corrosion measurements, including corrosion potential, polarization resistance, corrosion current, and impedance spectroscopy under saline conditions.

In this chapter, we represent polymer-layered silicate (PLS) nanocomposite materials (including conjugated polymers and non-conjugated polymers) as model coatings to demonstrate the advanced anticorrosive properties of layered silicate-based polymeric coatings by performing a series of electrochemical corrosion measurements.

2. Structure of layered silicates (clay)

The layered silicates commonly used in nanocomposites belong to the structural family known as the 2:1 phyllosilicates. Their crystal lattice consists of two-dimensional layers in which a central octahedral sheet of alumina or magnesia is fused to two external silica tetrahedron by the tip so that the oxygen ions of the octahedral sheet do also belong to the tetrahedral sheets. The layer thickness is around 1 nm, and the lateral dimensions of these layers may range from 300 Å to several microns or larger depending on the particular silicate. These layers organize to form stacks with a regular Van Deer Waals gap between each layer called the interlayer or the gallery. Isomorphic substitution within the layers (for example, Al_{3^+} replaced by Mg_{2^+} or by Fe_{2^+} , or Mg_{2^+} replaced by Li^+) generates negative charges that are counterbalanced by alkali or alkaline earth cations situated in the interlayer. As the forces that hold the stacks together are relatively weak, the intercalation of small molecules between the layers occurs readily [Theng, 1974]. In order to render these hydrophilic phyllosilicates more organophilic, the hydrated cations of the interlayer can be exchanged with cationic surfactants such as alkylammonium or alkylphosphonium (onium). Becouse the modified clay (or organoclay) is organophilic, its surface energy is lowered and is more compatible with organic polymers. These polymers may be able to intercalate within the galleries under well-defined experimental conditions. Montmorillonite, hectorite, and saponite are the most commonly used layered silicates. Their structure is given in Fig.1, [Giannelis et al., 1999; Sinha-Ray & Okamoto, 2003] and their chemical formula are shown in Table 1. This type of clay is characterized by a moderate negative surface charge (known as the cation exchange capacity, CEC, expressed in mequiv./100 g). The charge of the layer is not locally constant but varies from layer to layer; therefore, it much be considered as an average value over the whole crystal. Proportionally, even if a small part of the chargebalancing cations is located on the external crystallite surface, the majority of these exchangeable cations are located inside the galleries. When the hydrated cations are ionexchanged with organic cations such as more bulky alkylammoniums, it usually leads to a larger interlayer spacing. To describe the structure of the interlayer in organoclay, one must
know that, as the negative charge originates in the silicate layer, the cationic head group of the alkylammonium molecule preferentially resides at the layer surface, leaving the organic tail radiating away from the surface. In a given temperature range, two parameters then define the equilibrium layer spacing: the CEC of the layered silicate, driving the packing of the chains, and the chain length of the organic tail(s).



Fig. 1. Structure of 2:1 layered silicate showing two tetrahedral sheets of silicon oxide fused to an octahedral sheet of aluminum hydroxide.

Silicate	Location of isomorphous substitution	Formula
Montmorillonite	Octahedral	$M_x[Al_{4-x}Mg_x](Si_8)O_{20}(OH)_4^a$
Hectorite	Octahedral	$M_x[Mg_{6-x}Li_x](Si_8)O_{20}(OH)_4^a$
Saponite	Tetrahedral	$M_x[Mg_6](Si_{8-x}Al_x)O_{20}(OH)_4{}^a$

^a M = monovalent cation; x = degree of isomorphous substitution (between 0.5 and 1.3).

Table 1. Structure and chemistry of commonly used layered silicates

According to X-ray diffraction (XRD) data, the organic chains have been long thought to lay either parallel to the silicate layer, forming mono or bilayers, or, depending on the packing density and the chain length, to radiate away from the surface, leading to mono or even bimolecular tilted "paraffinic" arrangements [Lagaly, 1986], as shown in Fig. 2. A more realistic description has been proposed by Vaia et al., 1994, based on Fourier transform infrared (FTIR) spectroscopy experiments. By monitoring frequency shifts of the asymmetric CH₂ stretching and bending vibrations, they found that the intercalated chains exist in states with varying degrees of order. Generally, as the interlayer packing density or the chain

length decreases (or the temperature increases), the intercalated chains develop more disordered, liquid-like structure resulting from an increase in the gauche/trans conformer ratio. When the available surface area per molecule is within a certain range, the chains are not completely disordered but maintain some orientation order close to that in the liquid crystalline state, as shown in Fig. 3. Recently, this interpretation has been confirmed by molecular dynamics simulations in which a strong layering behavior with a disordered liquid-like arrangement that can evolve towards a more ordered arrangement by increasing the chain length has been found [Hackett et al., 1998]. As the chain length increases, the interlayer structure appears to evolve in a stepwise fashion, from a disordered to a more ordered monolayer, and then "jump" to a more disordered pseudo-bilayer.



Fig. 2. Orientations of alkylammonium ions in the galleries of layered silicates with different layer charge densities.



Fig. 3. Alkyl chain aggregation models (a) Short alkyl chains: isolated molecules, lateral monolayer; (b) intermediate chain lengths: in-plane disorder and interdigitation to form quasi-bilayers; (c) longer chain length: increased interlayer order, liquid crystalline-type environment.

3. Nanocomposite structures

In general, layered silicates have layer thickness on the order of 1 nm and very high aspect ratio (e.g., 10-1000). A few weight percent of layered silicates that are properly dispersed

throughout the polymer matrix create much higher surface area for polymer/filler interaction compared to conventional composites. Depending on the strength of interfacial interactions between the polymer matrix and the layered silicate (modified or not), three different types of polymer/layered silicate nanocomposites are thermodynamically achievable (Fig. 4)

- a. Intercalated nanocomposites: In intercalated nanocomposites, the insertion of a polymer matrix into the layered silicate structure occurs in a crystallographically regular fashion, regardless of the clay to polymer ratio. Intercalated nanocomposites are normally interlayered with a few molecular layers of polymer. Properties of the composites typically resemble those of ceramic materials.
- b. Flocculated nanocomposites: conceptually this is the same as intercalated nanocomposites. However, silicate layers are sometimes flocculated due to hydroxylated edge-edge interaction of the silicate layers.
- c. Exfoliated nanocomposites: In an exfoliated nanocomposite, the individual clay layers are separated in a continuous polymer matrix by an average distance that depends on the clay loading. Usually, the clay content of an exfoliated nanocomposite is much lower than that of an intercalated nanocomposite.



Fig. 4. Schematic illustration of three different types of thermodynamically achievable polymer/layered silicate nanocomposites.

4. Methods used for the synthesis of PLS nanocomposites

Intercalation of polymers in layered hosts, such as layered silicates, has proven to be a successful approach to synthesize PLS nanocomposites. The preparative methods are

divided into three main groups according to the starting materials and processing techniques

a. Intercalation of polymer or pre-polymer from solution (Fig. 5) [Xu et al., 2001; Yano et al., 1993; Aranda & Ruiz-Hitzky, 1992; Jimenez et al., 1997; Jeon et al., 1998; Tseng et al., 2001]: This is based on a solvent system in which the polymer or pre-polymer is soluble and the silicate layers are swellable. The layered silicate is first swollen in a solvent such as water, chloroform, or toluene. When the polymer and layered silicate solutions are mixed, the polymer chains intercalate and displace the solvent within the interlayer of the silicate. Upon solvent removal, the intercalated structure remains, resulting in PLS nanocomposites.



Fig. 5. Schematic representation of a PLS nanocomposite obtained by intercalation of polymer from solution.





b. In-situ intercalative polymerization method (Fig. 6) [Biswas & Sinha-Ray, 2001; Kojima et al., 1993; Usuki et al., 1993; Okamoto et al., 2000, 2001; Leu et al., 2002; Kim et al., 2003]: In this method, the layered silicate is swollen within the liquid monomer or a monomer solution so that polymer formation can occur between the intercalated sheets. Polymerization can be initiated either by heat or by radiation, by the diffusion of a

suitable initiator, or by an organic initiator or catalyst fixed through cation exchange inside the interlayer before the swelling step.

c. Melt intercalation method (Fig. 7) [Vaia & Giannelis, 1997; Vaia et al., 1993, 1995; Fornes et al., 2002; Wang et al., 2001; Usuki et al., 2002; Chisholm et al., 2002; Huang et al., 2000]: This method involves (statically or under shear), a mixture of the polymer and organically modified layered silicates (OMLS) above the softening point of the polymer. This method has advantages over either in situ intercalative polymerization and polymer solution intercalation. First, this method is environmentally benign due to the absence of organic solvents. Second, it is compatible with current industrial process such as extrusion and injection molding. The melt intercalation method allows the use of polymers that were previously not suitable for in-situ polymerization or solution intercalation.



Fig. 7. Schematic representation of a PLS nanocomposite obtained by direct melt intercalation.

5. Measures of corrosion prevention

Material selection

- a. Metals and alloys: The most common method for preventing corrosion is the selection of the proper metal or alloy for a particular corrosive service [Harple & Kiefer, 1953; Vernon, 1948].
- b. Metal purification: The corrosion resistance of a pure metal is usually better than that of one containing impurities or small amounts of other elements. However, pure metals are usually expensive and are relatively soft and weak. In general, pure metals are used in relatively few, special cases [Harple & Kiefer, 1953; Vernon, 1948].
- c. Nonmetallics: This category involves integral or solid nonmetallic construction (mainly self-supporting) and sheet linings or coverings of substantial thickness (different from paint coatings). The five general classes of nonmetallics are (1) rubbers (natural and

synthetic), (2) plastics, (3) ceramics, (4) carbon and graphite, and (5) wood [Harple & Kiefer, 1953; Vernon, 1948; Worspop & Kingsburf, 1950; Rohring, 1935].

- d. Changing mediums: Altering the environment provides a versatile means for reducing corrosion. Typical changes in the medium that are often employed include (1) lowering the temperature, (2) decreasing the velocity, (3) removing oxygen or oxidizers, and (4) changing the concentration. In many cases, these changes can significantly reduce corrosion, but they must be performed with care [Harple & Kiefer, 1953; Vernon, 1948; Welder & Partridge, 1954].
- e. Inhibitors: An inhibitor is a substance that, when added in small concentrations to an environment, decreases the corrosion rate. In a sense, an inhibitor can be considered a retarding catalyst. There are numerous inhibitor types and compositions. Most inhibitors have been developed by empirical experimentation, and many inhibitors are proprietary in nature thus, their composition is not disclosed. Inhibition is not completely understood because of these reasons, but it is possible to classify inhibitors according to their mechanism and composition [Harple & Kiefer, 1953; Vernon, 1948; Rosenfeld, 1981].

Cathodic and anodic protection

a. Cathodic protection: Cathodic protection was employed before electrochemistry had been developed. Humphrey Davy used cathodic protection on British naval ships in 1824. The principles of cathodic protection may be explained by considering the corrosion of a typical metal in an acid environment. Electrochemical reactions include the dissolution of the metal and the evolution of hydrogen gas:

 $M \rightarrow M^{n+} + ne$ $2H^{+} + 2e \rightarrow H_{2}$

b. Anodic protection: In contrast to cathodic protection, anodic protection is relatively new; it was first suggested by Edeleanu in 1954. This technique was developed using electrode kinetics principles and is somewhat difficult to describe without introducing advanced concepts of electrochemical theory. Simply, anodic protection is based on the formation of a protective film on metals by externally applied anodic currents [Acello & Greene, 1962; Locke & Sudbury, 1960].

Coatings

a. Metallic and other inorganic coatings: Relatively thin coatings of metallic and inorganic materials can provide a satisfactory barrier between a metal and its environment. The chief function of such coatings (aside from sacrificial coatings such as zinc) is to provide an effective barrier. Metal coatings are applied by electrodeposition, flame spraying, cladding hot dipping, and vapor deposition. Inorganics are applied or formed by spraying, diffusion, or chemical conversion. Spraying is usually followed by baking or firing at elevated temperatures. Metal coatings usually exhibit some formability, whereas the inorganics are brittle. In both cases a complete barrier must be provided. Porosity or other defects can result in accelerated localized attack on the basic metal because of two-metal effects [Draper, 1982; McCafferty et al., 1982; Moore & McCafferty, 1981; Potter et al., 1983].

Organic coatings: These involve a relatively thin barrier between the substrate material b. and the environment. Paints, varnishes, lacquers, and similar coatings protect more metal per ton than any other method for combating corrosion. Exterior surfaces are most common, but inner coatings or linings are also widely utilized. Approximately 2 billion dollars per year are expended in the United States on organic coatings. A myriad of types and products are involved, and some are accompanied by outlandish claims. Substantial knowledge of this complex field is required for successful performance. The best procedure for those who are inexperienced is to consult a reputable producer of organic coatings. As a general rule, these coatings should not be used where the environment would rapidly attack the substrate material [Garrett, 1964]. Aside from proper application, the three main factors to consider for organic coatings, listed in order of importance, are (1) surface preparation, (2) selection of primer or priming coat, and (3) selection of top coat or coats. Polymeric (or organic) coatings have been employed to protect metals against corrosion for a long time. The primary effect of a polymeric coating is to function as a physical barrier against aggressive species such as O2 and H⁺. However, not all polymeric coatings are permanently impenetrable, and once there are defects in the coatings, pathways will be formed for the corrosive species to attack the metallic substrate, and localized corrosion will occur. Therefore, as a second line of defense for corrosion, various pigments with a lamellar or plate-like shape, such as micaceous iron oxide and aluminum flakes, have been introduced into the polymeric coating to effectively increase the length of the diffusion pathways for oxygen and water as well as to decrease the permeability of the coatings. A number of electrochemical measurements have been used to evaluate the anticorrosion performance of polymeric coatings, including conjugated (e.g., polyaniline) or nonconjugated (e.g., polystyrene) polymers. Wei et al., 1995, demonstrated the anticorrosive performance of conjugated polyaniline and nonconjugated polystyrene by performing a series of electrochemical measurements of corrosion potential and corrosion current on the sample-coated cold-rolled steel (CRS) electrode under various conditions. Li et al., 1997, investigated the corrosion-resistance properties of polyaniline-coated mild steel in saline and acid by electrochemical impedance spectroscopy. Recently, PLS nanocomposites used as enhanced anticorrosion coatings have been reported by Yeh group [Yeh et al., 2001, 2002, 2003, 2004, 2005, 2006, 2007; Chang et al., 2006, 2007, 2008; Lai et al., 2007; Yu et al., 2004]. For example, conjugated polymers (e.g., polyaniline, polypyrrole, and poly(3-hexylthiophene)), thermoplastic polymers (e.g., poly(methyl methacrylate), polystyrene, poly(styrene-co-acrylonitrile), polysulfone, and polyacrylate), and thermosetting polymers (e.g., polyimide and epoxy) all had been blended with organo-modified clay or raw Na⁺-MMT clay through different preparative routes such as in-situ polymerization or solution dispersion, to make a series of novel advanced anticorrosion coatings based on a series of electrochemical corrosion parameter measurements of corrosion potential, polarization resistance and corrosion current at room temperature.

6. Anticorrosive properties

In a non-conjugated system, Yeh et al., 2002, reported a series of PCN materials that consisted of poly (methyl methacrylate) (PMMA) and layered MMT clay that were prepared by effectively dispersing the inorganic nanolayers of MMT clay in an organic PMMA matrix

via in-situ thermal polymerization. Organic methyl methacrylate monomers were first intercalated into the interlayer regions of organophilic clay hosts followed by a typical free-radical polymerization. The as-synthesized PCN materials were characterized by infrared spectroscopy, wide-angle powder XRD (Fig. 8), and transmission electron microscopy (TEM; Fig. 9). PCN coatings with low clay loading (e.g., 1 wt %) on CRS showed superior anticorrosion properties compared with those of bulk PMMA based on a



Fig. 8. Wide-angle powder X-ray diffraction patterns of organophilic clay, PMMA, and a series of PMMA-clay nanocomposite materials.



Fig. 9. Transmission electron microscopy of CLMA5.

series of electrochemical measurements of corrosion potential, polarization resistance, corrosion current, and impedance spectroscopy in 5 wt% aqueous NaCl electrolyte (Table 2 and Fig. 10–11). The molecular weights of PMMA extracted from PCN materials and bulk PMMA were determined by gel permeation chromatography (GPC) with tetrahydrofuran as an eluant. Effects of the material composition on the gas and water permeability (Fig. 12), optical clarity, and thermal stability of PMMA and PCN materials, in the form of both

free-standing films and fine powders, were also studied by molecular permeability analysis, ultraviolet-visible transmission spectra, differential scanning calorimetry, and thermogravimetric analysis, respectively.

compound code	feed com (wt PMMA	position %) MMT	inorganic content found in product ^b (wt %)	electrochemical corrosion measurements $\overline{F_{men}}$ (mV) $\overline{P_{m}}$ (kO:m ²) $\overline{F_{men}}$ (MPY) thickness ^c (m			s thickness ^c (µm)	
			······		тр (та тт,	-corr (- (011 (== =))
bare				-604	2.7	1.9×10^4	36.7	
PMMA	100	0	0	-485	3.2×10^{2}	1.2×10^{2}	2.3×10^{-1}	110
CLMA1	99	1	1.2	-379	9.2×10^2	4.5×10^{1}	8.0×10^{-2}	112
CLMA3	97	3	3.5	-278	6.4×10^{3}	9.4	1.8×10^{-2}	121
CLMA5	95	5	6.9	-78	7.5×10^3	5.7	1.1×10^{-2}	113
CLMA10	90	10	18.1	-19	$1.8 imes 10^4$	2.3	4.4×10^{-3}	117
CLMA-N10	90	10	22.1					

^a A saturated calomel electrode was employed as the reference electrode. ^b As determined form TGA measurements. ^c As measured by a digimatic micrometer.

Table 2. Relationships of the composition of PMMA–MMT clay nanocomposite materials with the Ecorr, Rp, icorr, and Rcorr measured using electrochemical methodsa



Fig. 10. Tafel plots for (a) uncoated, (b) PMMA-coated, (c) CLMA1-coated, (d) CLMA3-coated, (e) CLMA5-coated, and (f) CLMA10-coated CRS measured in 5 wt% NaCl aqueous solution.



Fig. 11. Nyquist plots of five CRS samples in 5 wt% NaCl aqueous solution (a) PMMA-coated, (b) CLMA1-coated, (c) CLMA3-coated, (d) CLMA5-coated, and (e) CLMA10-coated.



Fig. 12. Permeability of H_2O and O_2 as a function of the MMT clay content in the PMMA–clay nanocomposite materials.

According to the results above, the enhanced corrosion protection effect of PMMA nanocomposites compared to bulk PMMA might have resulted from dispersing silicate nanolayers of clay in the PMMA matrix to increase the tortuosity of oxygen gas diffusion pathways.



Fig. 13. Wide-angle powder X-ray diffraction patterns of organophilic clay, polyaniline, and a series of PMMA-clay nanocomposite materials.

In conjugated system, Yeh et al., 2001, investigated a series of nanocomposite materials consisting of an emeraldine base of polyaniline and layered (MMT) clay that were prepared by effectively dispersing the inorganic nanolayers of MMT clay in an organic polyaniline matrix via in-situ polymerization. Organic aniline monomers were first intercalated into the interlayer regions of organophilic clay hosts and followed by a one-step oxidative polymerization. The as-synthesized polyaniline–clay lamellar nanocomposite materials were characterized by infrared spectroscopy, wide-angle powder XRD (Fig. 13), and TEM (Fig. 14). Polyaniline–clay nanocomposites in the form of coatings with low clay loading (e.g.,

0.75 wt%) on CRS showed superior corrosion protection compared to those of conventional polyaniline based on a series of electrochemical measurements of corrosion potential, polarization resistance, and corrosion current in 5 wt% aqueous NaCl electrolyte (Fig. 15).



Fig. 14. TEM of CLAN3: with exfoliated single, double, and triple layers and a multilayer tactoid.



Fig. 15. Tafel plots for (a) uncoated, (b) PANI-coated, (c) CLAN025-coated, (d) CLAN05-coated, and (e) CLAN075-coated CRS measured in 5 wt% NaCl aqueous solution.

The molecular weights of polyaniline extracted from polyaniline-clay nanocomposite materials and bulk polyaniline were determined GPC. Effects of the material composition on

the gas barrier property (Fig. 16), thermal stability, and mechanical strength of polyaniline and polyaniline–clay nanocomposite materials, in the form of both fine powders and freestanding films, were also studied by gas permeability measurements, differential scanning calorimetry, thermogravimetric analysis, and dynamic mechanical analysis.



Fig. 16. Permeability of O_2 , N_2 , and air as a function of the MMT clay content in the polyaniline–clay nanocomposite materials.



Fig. 17. (a) Redox behavior of EET40-, EET10-, and EET0-coated Pt foil electrode measured in $1.0M H_2SO_4$ aqueous solution. (b) Tafel plots for EET40, EET10, EET0-coated and bare CRS electrodes measured in 5 wt% NaCl aqueous solution.

Huang et al., 2009, reproted a series of electroactive epoxy thermosets (EETs) containing conjugated segments of electroactive amino-capped aniline trimer (ACAT) units that were successfully prepared and characterized. Furthermore, the redox behavior of as-prepared EET materials was identified by electrochemical cyclic voltammetry studies. Higher concentrations of ACAT components in the corresponding as-prepared EETs led to remarkably enhanced corrosion protection effects on CRS electrodes based on sequential electrochemical corrosion measurements in 5 wt% NaCl supporting electrolyte (Fig. 17). The mechanism for the enhancement of corrosion protection of EET coatings on CRS electrodes might be attributed to the redox catalytic capabilities of ACAT units that existed in EETs, leading to the formation of passive metal oxide layers, as further evidenced by SEM and ESCA studies (Fig. 18–20).



Fig. 18. SEM image of (a) polished CRS metal and the surface of the (b) EET40 coating on the CRS metal.



Fig. 19. ESCA Fe 2p core spectrum of EET40.



Fig. 20. Schematic diagram of mechanism of the CRS passivation by EET coatings.

In conjugated polymers used for anticorrosion, higher concentration of conjugated ACAT units in as-prepared led to higher redox currents in the CV studies. Corrosion protection of EET coatings cast onto CRS electrodes was systematically investigated by performing sequential electrochemical corrosion measurements under saline conditions. Electrochemical corrosion experimental results showed that higher concentrations of ACAT segments in asprepared EETs resulted in better corrosion protection efficiency of the corresponding sample-coated CRS electrode. The remarkable enhancement of corrosion protection for EET coatings on CRS electrodes might probably be attributed to the redox catalytic (i.e., electroactivity) properties of conjugated ACAT units in the as-prepared electroactive EETs, leading to the formation of passivation metal oxide layers, as demonstrated by SEM and ESCA studies. The passive oxide layer is predominately composed of Fe_2O_3 , above a very thin Fe_3O_4 layer.

7. Conclusion

Smectite clays can be effective reinforcing agents in the synthesis of polymer/layered silicate nanocomposites that display superior properties, even at low clay content (<3 wt%). Nanocomposites show enhanced physical properties even with a small amount of added clay, because the nanoscale dimensions of the clay particles yield a large contact area between the polymer matrices and the filler. The structure of clays, with layers of high aspect ratio, also imparts excellent barrier that provide low gas permeability and enhanced anticorrosive properties.

Anticorrosive properties of non-conjugated polymer nanocomposites with layered silicates have been discussed herein. The as-prepared nanocomposites, in the form of coatings, showed advanced protection against corrosion on CRS coupons compared to bulk polymers based on a series of standard electrochemical corrosion measurements, including corrosion potential, polarization resistance, corrosion current, and impedance spectroscopy. The enhanced corrosion protection effect of nanocomposites compared to bulk polymers might have resulted from dispersing silicate nanolayers of clay in the polymer matrix to increase the tortuosity of diffusion pathway for H_2O and O_2 molecules and is further evidenced by the O_2 and H_2O permeability studies on the free-standing film of as-prepared nanocomposites.

It is noteworthy to mention that the investigations on the corrosion protection efficiency of coujugated polymer-layered silicate nanocomposite coatings were divided into two separate phases. First, neat conjugated polymeric coatings significantly enhanced corrosion protection on CRS electrodes compared to non-conjugated polymeric coatings, and this might be attributed to the redox catalytic property of electroactive aniline trimers in the formation of passive layers of metal oxides. Second, the advanced anticorrosive properties of conjugated polymer coatings were revealed by the introduction of layered silicate into the matrix to form conjugated polymer-layered silicate nanocomposite materials.

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Nd-Fe-B Nanocomposite Thin Films: Influence of the Additions on the Structure and Hard Magnetic Properties

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1. Introduction

Nd-Fe-B thin films have been extensively investigated as promising candidates for Micro-Electro-Mechanical Systems (MEMS) and in monolithic microwave integrated circuits (Walther et al., 2009, 1991; Lemke et al., 1995).

The Nd-Fe-B nanocomposite hard magnetic materials consist of suitably nanodispersed hard (i.e. $Nd_2Fe_{14}B$) and soft (i.e. α -Fe or Fe₃B) phases that are exchange coupled (Ao et al., 2006) and confer them specific magnetic properties with potential great impact on the permanent magnet market, such as enhanced technical performances (Wang et al., 2007) and low cost. Thus, in nanocomposite magnets, the best properties of the soft and hard magnetic phases are combined via exchange coupling on a nanometric scale (Ghidini et al., 2007).

The crystallographic structure of the nanocomposite hard magnetic magnets plays a more important role in controlling the magnetic properties than in single-phase magnets (Cui et al., 2000). Thus, the refinement of the microstructure and uniform distribution of the component phases are essential to obtain high coercivity, H_{cr} and high maximum energy products $(BH)_{max}$ (Chen et al., 2006). The optimization of microstructure and magnetic properties of Nd-Fe-B films can be obtained by compositional and phase modifications with additions of dopant elements (Jiang and O'Shea, 2000). Many metallic elements have been added to the ternary Nd-Fe-B system with the aim of improving the microstructure and magnetic properties (Cui et al., 2000; Chang et al., 2008, 2009). The Nd-Fe-B thin films deposited on substrates maintained during deposition at room temperature, in as-deposited state and after thermal treatments at temperatures below 550°C, have amorphous structure. During the annealing at higher temperatures, high melting point metal dopants (i.e. Nb, Zr, Mo, Ti, V, etc) act as nuclei for crystallization process, thus impeding grain growth upon initial annealing. Low melting point metal dopants (i.e. Cu, Al, Ga, In, Zn, etc) surround the magnetic phase grains in the course of crystallization, hindering their growth. Thus, in Nd-Fe-B alloys with the best magnetic properties, either or both types of such elements are usually added (Shandong et al., 2002; Chang et al., 2009). In order to enhance the intrinsic properties of the magnetic phases, other elements, such as rare-earth elements (i.e. Dy, Pr, La, Tb, Sm), are partially substituted for Nd (Shandong et al., 2002; Liu et al., 2003), transition elements, (i.e. Co, Mn), are partially substituted for Fe (Cui and O'Shea, 2003; Cui and O'Shea, 2004), and C partially replaces B (Ishii et. al., 2007).

Nanocomposite magnets exhibit a high remanence, M_r , and a large coercive field, H_{cr} if hard and soft phases are adequately exchange coupled. Remanence enhancement was observed in multilayered (α -Fe, Fe₃B)/Nd-Fe-B magnets because of the exchange coupling between soft and hard magnetic phases (Liu et al., 2003). Various multilayered systems, such as α -Fe/Nd₂Fe₁₄B (Cui et al., 2000; Wang et al., 2007), Fe₃B/Nd₂Fe₁₄B (Rajasekhara et al., 2008) or Fe-Co/Nd₂Fe₁₄B (Ao et al., 2006), with different thickness of constituent layers and grain size ratio of soft and hard magnetic phases were tested to determine the most optimum morphology of thin-film nanocomposite magnets with enhanced remanence.

As compared to isotropic single-phase nanocrystalline Nd-Fe-B magnets, the coercive field obtained in two-phase systems is rather low. Recent studies demonstrated that the addition of different transition metal elements with high and low melting points to the ternary Nd-Fe-B alloy is an effective method also for the hard magnetic properties improvement (Cui et al., 2000; Tsai et al., 2002; Ping et al., 2000; Shull, 2007).

The additives or substitutions were either included either within the Nd-Fe-B films volume or by stratification as spacer layers. The microstructure and magnetic properties of the multilayered systems can be well controlled by varying the thickness of the soft and hard magnetic layers. Studies have been also reported on the influence of singular and multiple additions such as, Co, (Nb and Cu), and (Fe and Si), the thickness of component layers and annealing conditions on the structure and hard magnetic properties of multilayered [Nd-Fe-B/(Nb-Cu)]×n (a-Chiriac et al., 2007), [Nd-Fe-B-Nb-Cu/Co]×n (b-Chiriac et al., 2007) and [Nd-Fe-B-Nb-Cu/Fe-B-Si]×n (Chiriac et al., 2008) thin films. The Nb and Cu additions act in the sense of impeding the grain growth and promoting the formation of nucleation sites, respectively (Chiriac et al., 1999; Tsai et al., 2002, 2000; Wang et al., 2005; Ping et al., 2000 and 1999), Co increases the Curie temperature and boosts the crystallization and grain growth (Cui and O'Shea, 2003, 2004; Jurczyk and Jakubowicz, 2000; Chiriac and Marinescu, 1998), whereas Si slightly increases the Curie temperature and improves the rectangularity of the demagnetization curves (Coey, 1996; Xiong et al., 2002).

In this chapter the results with regard to the magnetic properties of Nd-Fe-B nanocomposite permanent magnet thin films (single layer and multilayer) with addition of Cu, Nb and Si, respectively, and Co substitution for Fe, are presented. The results concerning the effect of the thickness of constituent layers and annealing conditions on the structure, hard magnetic properties and exchange coupling between hard and soft magnetic phases composing the nanocomposite Nd-Fe-B thin films are comparatively discussed. The thermal stability evolution as a result of thermal cycling in the temperature range 25-350°C for Nd-Fe-B, Nd-Fe-B-Nb-Cu and [Nd-Fe-B-Nb-Cu/Co]×3 thin films is also presented. The influence of the ageing for different periods of time at 150°C, on the losses in coercivity, H_{c} and remanent magnetization, M_r , has been also studied and will be discussed in detail (Chiriac et al., 2009).

2. Nd-Fe-B nanocomposite thin films processing

Generally, the Nd-Fe-B thin films are prepared by different vacuum deposition techniques, such as magnetron r.f/d.c sputtering, ion-plasma sputtering, molecular beam epitaxy, laser ablation, etc.

Our buffer/Nd-Fe-B/capping thin-film samples without or with additions (single layer and multilayer) were prepared, in vacuum, by sequential deposition in a conventional deposition system (Laboratory Sputtering Plant Z – 400) using r.f sputtering and electron beam evaporation techniques. The simple or composite sputtering targets were mounted on

two separate guns and were made as follows: a disc of stoechiometric Nd-Fe-B alloy with Nd and other addition chips on its surface; a disc of specific materials for 'buffer' or 'capping' layers (i.e. Ta, Nb or Nb-Cu); a disc of Nb-Cu combination or Fe-Si-B alloy, for spacer layer.

Usually, during Nd-Fe-B thin film deposition, a Nd supplementary amount is required to be added to compensate oxidation of Nd. Generally, compositional changes of samples were made by modifying the surface of the components on the sputtering targets, or by modifying the thicknesses of hard and soft layers of multilayer systems.

The soft magnetic (i.e. Co) thin films were prepared in vacuum using electron beam evaporation technique.

The substrate temperature during the deposition of thin films is the first important parameter of this technological process. The Nd-Fe-B films are amorphous when the substrate temperature is lower than the main phase $Nd_2Fe_{14}B$ crystallization temperature (Lileev et al., 2002).

The sputtered samples were deposited, at room temperature, in high purity (99.999%) argon (Ar) atmosphere at working presure of about 10^{-2} mbar. The background pressure of the vacuum chamber was about $2x10^{-6}$ mbar. The distance between sputtering target and substrates was of about 3.2 cm.

The thickness of the individual layers prepared by electron beam evaporation techniques (i.e. Co), was controlled during the deposition process by a quartz-crystal deposition monitor (FTM 6 Film Thickness Monitor) having a resolution of about 0.1 nm. When r.f sputtering was used as deposition technique, the thickness of the individual films was verifiyed 'ex-situ' by the KLA Tencor Alpha – Step IQ Profilometer. Thus, the thickness of each sputtered layer from multilayer system was monitored during the deposition process by controlling the sputtering time.

The magnetic and thermo-magnetic measurements were performed at room temperature and in the temperatures range $25 \div 900$ °C, respectively, by a vibrating sample magnetometer (Lake Shore VSM 7410) with a maximum magnetic field of 31 kOe applied parallel with the film plane.

The crystallographic structure was investigated using X-ray diffraction (XRD) analysis. A X-ray diffractometer (Bruker AxS GmbH - D8 Advance) with a monochromatized Cu-K α radiation was used in a Bragg-Brentano arrangement. The Warren-Averbach method (Klug and Alexander, 1974) was used to estimate the crystalline grain sizes (error of ± 15%).

The film composition of the individual films was obtained by using the SEM/EDS (Scanning Electron Microscopy – JEOL JSM 6390, and associated Energy – Dispersive Spectrometry) technique.

The morphology of the samples was investigated by Transmission Electron Microscopy (TEM) technique using molybdenum 'microscope grids' coated with an evaporated carbon thin film having the thickness between 8 and 10 nm.

The Nd₂Fe₁₄B/(α -Fe, Fe₃B) nanocomposite structure is usually obtained by controlled crystallization of amorphous phase. DSC studies shown that nucleation temperatures of the α -Fe and Nd₂Fe₁₄B phases are of about 525°C and 590°C, respectively (Cui et al., 2005). In order to crystallize the Nd₂Fe₁₄B and soft magnetic phases and obtain good hard magnetic properties, the Nd-Fe-B thin-film samples can be subjected after deposition, to two types of annealing procedures. Thus, the as – deposited samples can be treated in vacuum (p = 4 x 10⁻⁴ Pa) by rapid (30 second) or standard (10-30 minutes) annealing at temperatures between 550°C and 780°C. A rapid annealing of about 30 s at a higher temperature allows more nucleation centers to form and grow during the crystallization process of the as-

deposited films. Comparing with a longer time and lower temperature annealing, it is expected that a rapid annealing would lead to more uniform grain size for both the hard and soft phases and sharper interface boundaries (Cui and O'Shea, 2004).

Other types of thermal treatment procedures have been also proved to be effective in improving the magnetic performance of nanocomposite permanent magnet materials. Cui and co-workers (2005) studied the influence of magnetic field annealing on the magnetic properties of Nd_{2.4}Pr_{5.6}Dy₁Fe₈₄Mo₁B₆ ribbons. Compared with the sample annealed without a field, there is a noticeable improvement in the magnetic properties for the magnetically annealed samples, especially of the energy product $(BH)_{max}$. This improvement is a result of the enhanced crystallographic texture, nanostructure refinement, and in-plane uniaxial magnetic anisotropy. Similar effect may be expected in thin films.

In the course of our own research studies, different compositions of Nd-Fe-B target were tested in view of obtaining the Nd-Fe-B thin films with optimum hard magnetic properties. The composition of the Nd-Fe-B thin films was adjusted by changing the numbers of Nd chips on the surface of the sputtering target. The optimum hard magnetic properties of Nd-Fe-B thin films were obtained when the following composition of sputtering target was used: disc of $Nd_{12}Fe_{82}B_6$ alloy with the diameter of 7.5 cm having on its surface Nd chips with the a total area of about 4.9 cm² and B chips with the a total area of about 5.3 cm². The composition of Nd-Fe-B(540nm) film obtained by SEM/EDS technique is as follows: Fe 77.23 at.%, Nd 15.02 at.%, B up to 100 at.%.

The structure and magnetic properties of thin films can be strongly influenced by the interaction between the film and the substrate or (if present) buffer layer. Capping layer has also an important influence on the hard magnetic characteristics of Nd-Fe-B thin films. Several materials (such as Cr, Mo, Nb, Ta, Ti, V, etc.) were used between the Nd-Fe-B layer and the substrate to protect the Nd-Fe-B from oxidation by any oxygen in oxide form located on the substrate, and to control the growth of the Nd₂Fe₁₄B phase. Usually, same materials are used as protective over layers since they are mechanically hard and form stable oxides, and moreover, the rare earths (i.e. Nd) have a low solubility in the respective oxide compounds (Jiang and O'Shea, 2000).

In our experiments, all the samples were sandwiched between two Ta layers with the thickness of 40 nm and 20 nm, which were used as buffer layer and capping layer, respectively. Occasionally, we used two Nb-Cu films with the thickness of about 20 nm as buffer layer and capping layer.

3. Relationship between the magnetism of Nd₂Fe₁₄B/(α -Fe, Fe₃B) and microstructure

In nanocomposite permanent magnets the structure plays an important role on the magnetic properties than in single phase magnets. Generally, the optimum nanostructure of thin-film nanocomposite magnets consists of uniformly distributed hard magnetic and soft magnetic or non-magnetic phase grains.

The permanent magnet properties of nanocomposite alloys based on rare earth – transition metals are determined through the magnetic hardening of the soft magnetic grains based on Fe by the Nd₂Fe₁₄B hard magnetic neighboring grains. The optimum behavior of Nd₂Fe₁₄B/(α -Fe, Fe₃B) nanocomposite alloys as hard magnetic materials originates in the magnetic interactions between the uniformly distributed hard (Nd₂Fe₁₄B) and soft (α -Fe, Fe₃B and other) magnetic grains.

Homogenous and textured nanostructures are essential for the achievement of high maximum energy product $(BH)_{max}$ in nanocomposites (Cui et al., 2005; Manaf et al., 1993). At the same time, the grain size of the soft phase reduced at the same order of magnitude as the double domain wall width of the Nd₂Fe₁₄B phase allows the exchange interaction between both magnetic phases, thus preserving a high coercivity. In order to achieve this criterion, special attention is necessary to be paid to the formation of the nanocrystalline phases including compositional peculiarities and material preparation procedures (Manaf et al., 1993).

Because the magnetization reversal starts at the grain boundaries where a strongly nonuniform magnetic state exists, the intrinsic magnetic properties of this region strongly influence the remanent magnetization and the coercive field of two phase nanocomposite magnets. The remanent amorphous intergranular phase is expected to reduce the exchange interactions between the hard and soft grains, leading to an improved coercive field (Schrefl et al., 2000).

Fukunga and co-workers (1999) also proposed a two-phase microstructure consisting of Nd-Fe-B and α -Fe or Fe₃B grains embedded within a residual amorphous phase. With the same reason as described above, increase of the coercive field without a significant loss of the remanent magnetization enhances the energy density product (Schrefl et al., 2000).

Thin-film NdFeB/ α -Fe nanocomposite magnets consisting of dispersed hard and soft magnetic phases with the grain size in the 10-30 nm range have been reported (Shindo et al., 1997; Yang and Kim, 1999) with high reduced remanent magnetization and magnetic energy product. These materials have wide application as permanent magnets and are useful in micro-mechanical devices (Walther et al., 2009) and may have numerous applications in magneto-electronic devices.

Generally, all the as-deposited and below 550°C annealed Nd-Fe-B thin films have H_c values of up to 200 Oe. Annealing at 550°C or higher, results in the formation of the hard Nd₂Fe₁₄B phase responsible for the coercivity increase. XRD investigations demonstrate that the Nd-Fe-B thin films annealed at temperatures of about 550°C are composed of a structural mixture in which a small amount of α -Fe and Nd₂Fe₁₄B nanocrystallines are embedded in an amorphous matrix. Annealing at 650°C or higher for 20 minutes leads to the formation of a composite structure consisting of α -Fe and Nd₂Fe₁₄B phases.

To obtain a more ideal structure with a uniform distribution of the soft and hard phases, a multilayer system with alternating soft and hard magnetic layers was prepared by using of successive vacuum depositions. In such materials there is a trade-off between the magnetization increase and coercivity decrease as the amount of the soft phase is increased (Cui and O'Shea, 2004). In this nanostructured form there is a large interface contact area between soft and hard grains leading to a strong interface magnetic exchange effect which couples the soft and hard component phases. If the size of the soft phase is comparable with the double domain wall thickness of the hard phase, the two phases reverse together under the influence of a reverse applied field (Cui and O'Shea, 2003).

In contrast to bulk magnets, the structure of the multilayer materials can be easily controlled during the preparation process by properly arranging different layers, adjusting the thickness of the layers of the hard and soft phases, and annealing at the proper temperatures. This leads to an optimized average grain size and grain-size distribution (Ao et al., 2006). In comparison with the single-layer, the remanent magnetization of the multilayer magnets was found to increase noticeably (Liu et al., 2003).

Refinement of the Nd-Fe-B films microstructure to less than 40 nm is essential to obtain the high coercivity and high-energy product $(BH)_{max}$. (Miyoshi et al., 2000). A number of specific factors including sample composition, preparation and annealing conditions can affect the microstructure of the thin films and their magnetic properties A good control of the nanocomposite thin films microstructure can be achieved by architecture (stratification of the hard magnetic layer with magnetic or non-magnetic film used as spacer layer; thicknesses of layers; embedding of hard magnetic grains in a magnetic or non-magnetic matrix) and by additions.

4. Influence of additions on structural and hard magnetic properties

The design of the nanocomposite materials depends on a great number of factors, such as the crystallite size, texture, interfaces volume, etc., which are significantly influenced by the composition, deposition methods and process parameters.

Hirosawa and co-workers (1993) reported that the modification of the alloy composition by microalloying is an effective way of improving the hard magnetic properties of the Fe₃B/Nd₂Fe₁₄B nanocomposite magnets. The main effects of additives and substitutions on the magnetic properties of the nanocomposite magnets originate from modifications of the grain sizes of the soft and the hard magnetic phases (Cui et al., 2000).

Typically, the improvement in the magnetic properties of nanocomposite magnets is a result of the enhanced crystallographic texture, nanostructure refinement, and uniaxial magnetic anisotropy enhancement (Cui et al., 2005).

A commonly way for the preparing of the Nd₂Fe₁₄B/(α -Fe, Fe₃B) nanocomposite magnetic materials is to crystallize an amorphous precursor phase into a mixture of hard and soft magnetic phases (Chang et al., 1999; Cui et al., 2003). In Nd-Fe-B nanocomposite magnets, the replacement of α -Fe with Fe₃B improves the coercive field, H_c , but deteriorates the loop shape (Schrefl and Fidler, 1999). For Nd₂Fe₁₄B/ α -Fe nanocomposite magnetic materials, the reduction of coercive field is attributed to the emergence of α -Fe after annealing. Because, the α -Fe and the metastable phases (such as Nd₃Fe₆₂B₁₄) usually precipitate from the amorphous precursor earlier than the Nd₂Fe₁₄B phase, and moreover, the α -Fe grains tend to grow coarse during the decomposition of metastable phase therefore leading to weakening of the intergrain exchange coupling, it is important to find a way to change the crystallization behavior of the amorphous phase and to restrain the excessive growth of the soft and hard magnetic grains (Withanawasam et al., 1994).

Nanocomposite permanent magnets require nanostructured grain sizes, especially for the soft magnetic phase. In addition to the grain size of α -Fe, the grain size of Nd₂Fe₁₄B hard magnetic phase is another important factor in determining the magnetic properties of Nd-Fe-B nanocomposite materials (Wang et al., 2007). The optimum average grain size of the α -Fe is different for various element substitutions (Cui et al., 2000).

The exchange-coupling interactions between soft and hard grains increase the average anisotropy of soft magnetic grains and decrease the one of hard magnetic grains. In order to get higher effective anisotropy between magnetically soft and hard magnetic grains, the grain size of hard magnetic grain should not be less than 25 nm, and the grain size of soft magnetic grain should be about 10 nm (Sun et al., 2008). The control of grain growth in magnet processing is generally accomplished with non-magnetic additives, at the expense of forming grain boundary phases that reduce interfacial coupling and the overall magnetization

(Hadjipanayis, 1999; Jiang et al., 2004). The optimum average grain size is different for various element substitutions (Cui et al. 2000).

Generally, the additives can be embedded in magnetic thin film volume by two ways: (1) the stratification of magnetic film using additive film as spacer layers and (2) the inclusion of additives direct in the film volume during deposition by co-deposition (i.e. co-sputtering; sputtering out of composite targets). Many metallic elements can be added to the ternary Nd-Fe-B system with the aim of enhancing the magnetic properties. Generally, high melting point metals such as Zr, Nb, Mo, Ti, etc, act as nuclei for crystallization which emerge from the amorphous matrix in the primary stage of crystallization, thus impeding grain growth on initial annealing. These types of additions lead to the refinement of both Nd₂Fe₁₄B and α -Fe phases (Zhang et al., 2009; Chang et al., 2008; Wang et al., 2005 and 2007). Low melting point metals such as cooper (Cu) can reduce the crystallization temperature of the alloy (Ping et al., 1999).

4.1 Influence of Nb and Cu additions

Minor addition of cooper (Cu) to $Nd_{4.5}Fe_{77}B_{18.5}$ alloy is effective in refining the $Fe_3B/Nd_2Fe_{14}B$ nanocomposite microstructure that is produced by crystallization of amorphous phase. While single addition of niobium (Nb) shows adverse effect on the grain size of the nanocomposite, combined addition of Cu and Nb to $Nd_{4.5}Fe_{77}B_{18.5}$ shows beneficial effect on the nanocomposite microstructure and the hard magnetic properties. On the other hand, the single addition of Cu is not beneficial in refining the α -Fe/Nd₂Fe₁₄B nanocomposites (Ping et al., 2000). Since, as previously mentioned, the α -Fe/Nd₂Fe₁₄B nanocomposites show a higher coercivity than Fe₃B/Nd₂Fe₁₄B, thus it was worth exploring the effect of Cu and Nb additions to α -Fe/Nd₂Fe₁₄B nanocomposites as well.

Refinement of the Nd-Fe-B films microstructure to less than 40 nm for the hard grains is essential to obtain the high coercivity and high-energy product (Miyoshi et al., 2000). A number of specific factors including sample composition, spacer layer material and annealing temperature can affect the structure of the thin films and its magnetic properties (Jiang and O'Shea, 2000). Among the metallic elements which can be added to the ternary Nd-Fe-B system with the aim of enhancing the magnetic properties, Cu and Nb are known to act in the sense of promoting the formation of nucleation sites and decreasing the crystalline grain growth, respectively (Ping et al., 2000). The grain refinement by Nb substitution may be responsible for the increase of coercivity, H_{cr} and remanence, M_r .

In this context, results concerning the influence of the composition and thickness of the Nb-Cu spacer layer on the microstructure and magnetic properties of multilayer [NdFeB/NbCu]xn films are presented in the following (a-Chiriac et al., 2007). A comparison between the microstructure and magnetic characteristics of Nd-Fe-B, Nd-Fe-B-Nb-Cu and [NdFeB/NbCu]xn and thin films is also presented.

The coercivity, H_c , is an extrinsic magnetic property which is not only influenced by the chemical composition, substrate temperature and crystalline anisotropy, but also depends on the microstructure that is significantly influenced by the deposition and annealing processes.

The XRD analysis reveled that the Nd-Fe-B and [NdFeB/NbCu]xn samples in as-deposited state and after thermal standard treatment at temperatures below 550°C, have an amorphous structure. After annealing between 550 and 750°C, the Nd-Fe-B and [NdFeB/NbCu]xn thin films undergo a transition from amorphous to crystalline structure and the main diffraction peaks are identified as corresponding to Nd₂Fe₁₄B tetragonal phase.

The magnetic measurements showed that for low annealing temperatures between 500 and 600°C, the films have an increased value of remanence ratio ($M_{t/}/M_s = 0.7$) and a reduced coercivity due to exchange-coupling interaction between the Nd₂Fe₁₄B grains. For annealing temperatures over 610°C, for different periods of time, the grains reach sizes between 40 and 60 nm and some Nb- and Cu-secondary phases appear. For these annealed samples the values of the coercive field, H_{cr} and the remanence ratio, M_{tr}/M_{sr} increase.

Figure 1 shows the dependence of the magnetic properties on the annealing time for annealed NbCu(20nm)/[NdFeB(180nm)/NbCu(5nm)]x3/NbCu(20nm) thin film annealed at 610°C.



Fig. 1. The dependence of the magnetic properties on the annealing time for multilayer NbCu(20nm)/[NdFeB(180nm)/NbCu(5nm)]x3/NbCu(20nm) thin films.

The annealing time below 20 minutes are not enough to promote full crystallization, while time above 20 minutes lead to excessive grain growth. The optimal annealing time was 20 minutes.

Table 1 shows the evolution of main magnetic characteristics of the NbCu(20nm)/[NdFeB (t₁)/NbCu]xn/NbCu(20nm) films as a function of different thickness (t₁) for Nd-Fe-B layers, after annealing for 20 minutes at different temperatures (T_a). The thickness of the Nb-Cu spacer layer is constantly maintained at about 5 nm. The optimal Nd-Fe-B layer thickness was 180 nm.

In Table 1 can be observed that for NbCu/[NdFeB(180nm)/NbCu (5nm)]x3/NbCu sample annealed at temperatures T_a between 610 and 650°C, the coercive field, H_c , increases from 15.1 kOe to 17 kOe due to the domain wall pinning effect by the Nb- and Cu-based precipitated fine grains, and the saturation magnetization, M_s , also increases from 63 emu/g to 65 emu/g due to the crystalline structure improvement.

The better hard magnetic characteristics are obtained for NbCu/[NdFeB(180nm)/NbCu (5nm)]x3/NbCu film annealed for 20 minutes at 650°C.

In Table 2, the comparative results concerning the hard magnetic characteristics for single layer NbCu(20nm)/NdFeB(540nm)/NbCu(20nm) and multilayer NbCu(20nm)/[NdFeB (180nm)/NbCu(t₂)]x3/NbCu(20nm) film with different thickness (t₂) of Nb-Cu spacer layer, after annealing for 20 minutes at 650°C, are presented.

Samples /	M _s (emu/g)			H _c (kOe)		
(an the theoriesses in finit)	T _a (°C)			T _a (°C)		
	610	650	670	610	650	670
NbCu/NdFeB(540)/NbCu	78.0	98.0	100.0	11.6	12.0	12.4
NbCu/[NdFeB(270)/NbCu(5)]x2/NbCu	76.0	97.0	99.0	12.3	12.8	11.8
NbCu/[NdFeB(180)/NbCu(5)]x3/NbCu	63.0	65.0	70.0	15.1	17.0	13.8
NbCu/[NdFeB(90)/NbCu(5)]x6/NbCu	58.5	59.2	60.1	12.8	15.3	13.2

Table 1. The main magnetic characteristics of the NbCu(20nm)/[NdFeB(t_1)/NbCu]xn /NbCu(20nm) films with different thickness for Nd-Fe-B layers, after annealing at different temperatures for 20 minutes.

Sample /	Ms	Hc	NA /NA
(all the thicknesses in nm)	(emu/g)	(kOe)	$1VI_{\rm r}/1VI_{\rm s}$
NbCu/NdFeB(540)/NbCu	98.0	12.0	0.60
NbCu/[NdFeB(180)/NbCu(3)]x3/NbCu	67.5	19.0	0.80
NbCu/[NdFeB(180)/NbCu(5)]x3/NbCu	65.0	17.0	0.50
NbCu/[NdFeB(180)/NbCu(6)]x3/NbCu	56.0	12.0	0.40
NbCu/[NdFeB(180)/NbCu(10)]x3/NbCu	44.0	11.6	0.44

Table 2. The magnetic characteristics of the NbCu(20nm)/NdFeB(540nm)/NbCu(20nm) film and multilayer NbCu(20nm)/[NdFeB(180nm)/NbCu(t_2)]x3/NbCu(20nm) film.

It can be observed that the better magnetic properties were obtained for a structure having n = 3 (NdFeB/NbCu) bilayers and a thickness of about 3 nm for the Nb-Cu thin film.

Figure 2 shows the electron micrographs for Nd-Fe-B film (Fig.2a) with the thickness of about 54 nm and NbCu(3nm)/NdFeB(54nm)/NbCu(3nm) film (Fig.2b) with a total thickness of about 60 nm, after annealing under vacuum, for 20 minutes at 650°C.

The micrograph of NbCu(3nm)/NdFeB(54nm)/NbCu(3nm) film presented in Fig. 2b reveals a definite and fine structure of Nd₂Fe₁₄B crystalline grains with dimensions of about 35 nm, as compared to grain sizes of Nd-Fe-B film (Fig. 2a) which are of about 60 nm.



Fig. 2. TEM micrographs of Nd-Fe-B film (a) and NbCu(3nm)/NdFeB(54nm)/NbCu(3nm) film (b), after annealing for 20 minutes at 650°C.

From XRD results, the average dimension of the crystalline grains for NbCu(20nm)/ NdFeB(540nm)/NbCu(20nm) sample annealed for 20 minutes at 650°C, is about 40 nm, and this large value is due to the larger thickness of Nd-Fe-B layer of about 540 nm.

Analyzing the presented results it can be observed that, the hard magnetic properties of multilayer [NdFeB/NbCu]xn thin films sensitively depend on the composition and thickness of the Nb-Cu spacer layer.

As compared to Nd-Fe-B single layer, the multilayer NbCu/[NdFeB(180nm)/ NbCu(3nm)]xn thin films with the thickness of the Nd-Fe-B layer of 180 nm and the thickness of the Nb-Cu layer of about 3 nm exhibit better hard magnetic characteristics such as, coercive force of about 19 kOe and remanence ratio of about 0.8.

Next, some results concerning the Nd-Fe-B with Ta as buffer and capping layers and Nb-Cu additive directly embedded in thin film volume are presented. For Ta/Nd-Fe-B-Nb-Cu/Ta films, the optimum hard magnetic properties have been obtained for following composition determined by SEM/EDS technique: Fe, 64.57 at.%, Cu, 1.81 at.%; Nb, 5.08 at.%; Nd, 13.21 at.%; Ta, 9.43 at.%; and B, up to 100 at.%. For this composition, the 'architecture' of the sputtering composite target is following: disk of $Nd_{12}Fe_{82}B_6$ alloy having on its surface chips with the areas of 4.9 cm² of Nd, 5.3 cm² of B, 4 cm² of Nb, and 1.1 cm² of Cu.

Table 3 shows the magnetic characteristics of the Ta(40nm)/NdFeBNbCu(540nm)/Ta(20nm) thin films annealed at different temperatures for 20 minutes.

Sample (all the thicknesses in nm)	Т _а (°С)	H _c (kOe)	M _r (emu/g)
Ta(40)/NdFeBNbCu(540)/Ta(20)	610	21.7	77.0
	630	22.1	84.5
	650	24.2	82.4
	680	24.0	53.5

Table 3. The magnetic characteristics of the Ta/NdFeBNbCu(540nm)/Ta thin films annealed at different temperatures for 20 minutes.



Fig. 3. The hysteresis loops for the Ta/NdFeBNbCu(540nm)/Ta, and multilayer NbCu/ [NdFeB(180 nm)/NbCu(3nm)]x3/NbCu films annealed for 20 minutes at 650°C.

Annealing between 610 and 630°C leads to an increase of the remanent magnetization, M_{ν} , values from 77 to 84.5 emu/g due to the exchange-coupling effect between the Nd₂Fe₁₄B grains. For samples annealed at these temperatures the coercive field value slightly increases. The better hard magnetic characteristics are obtained for samples annealed for 20 minutes at 650°C.

In Figure 3, the hysteresis loops for the Ta(40nm)/NdFeBNbCu(540nm)/Ta(20nm) single layer and multilayer NbCu(20nm)/[NdFeB(180nm)/NbCu(3nm)]x3/NbCu(20nm) thin film, annealed for 20 minutes at 650°C are comparatively presented. It can be observed that the use of Ta films as buffer and capping layers and of Nb-Cu additive directly embedded in the film volume during deposition by sputtering composite targets is very effective in enhancing the coercive field, H_{cr} and saturation magnetization of Ta(40nm)/NdFeBNbCu (540nm)/Ta(20nm) samples.

4.2 Influence of Co addition

Addition of cobalt (Co) to $Nd_2Fe_{14}B$ nanocomposite magnets results in an increase of the Curie temperature and can result in an improvement of hard magnetic properties. Small Co addition leads also to a small increase in magnetization (Matsuura et al., 1985). In (Nd,Pr)-(Fe,Co)-B alloys, a Co content of about 30% improves the thermal stability through enhanced Curie temperature but it may decrease the coercivity (Harland and Davies, 2000). Results concerning the influence of the simultaneous Nb-Cu and Co additions and the stratification effect on the microstructure and hard magnetic properties of multilayer Ta/

[NdFeBNbCu/Co]xn/Ta thin films (b-Chiriac et al., 2007) are described below. In Figure 4 the dependence of the coercive field, H_c , and saturation magnetization, M_{sr} on

the thickness of the Co layers for multilayer Ta/[NdFeBNbCu(180nm)/Co(t)x3/Ta thin films annealed for 20 minutes at 650° C is presented.



Fig. 4. The dependence of the hysteresis parameters on the thickness of the Co layers for Ta/ [NdFeBNbCu (180 nm)/Co(t nm)]×3/Ta films annealed for 20 minutes at 650°C.

The coercive field, H_{α} decreases for thicknesses of the Co layers of up to 4 nm, since the Co phase has a much lower anisotropy than $Nd_2Fe_{14}B$ phase and the average anisotropy of the coupled phases is decreased (Cui and O'Shea, 2004). For larger Co thickness, the coercive field presents an inexplicable increase up to 6 nm, reason for which an extended research effort is needed. It can be also observed that there is a gradual increase of the saturation magnetization with the increase of the thickness of the Co layers up to 4 nm, followed by a slow decrease for Co layers with the thickness of 6 nm. A similar behavior for the dependence of the saturation magnetization on the Co content was noticed in Nd-Fe-Co-B quaternary alloys, $R_2(Fe_{1-x}Co_x)_{17}$ pseudobinary systems, and $Fe_{1-x}Co_x$ binary systems (Matsuura et al., 1985). When Co substitutes Fe, the saturation magnetization increases slightly to a maximum (i.e., x = 0.1 for Nd₂(Fe_{1-x}Co_x)₁₄B and x = 0.4 for R₂(Fe_{1-x}Co_x)₁₇) and subsequently decreases for larger Co contents. For Ta/[NdFeBNbCu(180nm)/Co(t)]x3/Ta structure when the thickness of the Co layer is 4 nm, Co represents about 2.8% from the total volume of multilayer [NdFeBNbCu(180nm)/Co(4nm)]x3 system, which is the optimum content for the highest saturation magnetization. When the thickness of the Co layer is of 6 nm, the Co content from [NdFeBNbCu(180nm)/Co(6nm)]x3 system represents about 4.25%, and in this case the saturation magnetization decreases.

Table 4 compares the magnetic characteristics for Ta/[NdFeBNbCu(t)/Co(2nm)]xn/Ta system with different thickness (t) of NdFeBNbCu layers, annealed at different temperatures for 20 minutes.

Samples (all the thicknesses in nm)	T _a (°C)	H _c (kOe)	Mr (emu/g)
Ta/[NdFeBNbCu(270)/Co(2)]x2/Ta	610	23.2	69.6
	630	22.9	70.6
	650	20.1	70.6
	680	23.9	71.7
	700	23.5	84.5
Ta/[NdFeBNbCu(180)/Co(2)]x3/Ta	610	18.4	100.6
	630	18.7	94.2
	650	22.7	100.6
	680	22.5	79.2
	700	20.2	91.0
Ta/[NdFeBNbCu(90)/Co(2)]x6/Ta	610	13.0	94.2
	650	8.8	82.4
	680	13.1	75.0
	700	9.5	101.7

Table 4. The magnetic properties for Ta/[NdFeBNbCu(t)/Co(2nm)]xn/Ta system with different thickness of NdFeBNbCu layers annealed at different temperatures for 20 minutes.

It can be observed that Ta/[NdFeBNbCu(180nm)/Co(2nm)]x3/Ta films annealed at 650°C for 20 minutes, present the optimum hard magnetic properties for practical applications such as thin-film permanent magnets.

Figure 5 shows the thermomagnetic curves of the magnetic Ta/NdFeBNbCu(540nm)/Ta single layer and multilayer Ta/[NdFeBNbCu(180nm)/Co(2nm)]x3/Ta films after devitrification and crystallization treatments at 650°C for 20 minutes.



Fig. 5. The thermomagnetic curves of the Ta/NdFeBNbCu(540nm)/Ta and Ta/(NdFeBNbCu(180nm)/Co(2nm)]x3/Ta thin films, annealed at 650°C for 20 minutes.

From thermomagnetic curves, it can be observed that the multilayer Ta/[NdFeBNbCu (180nm)/Co(2nm)]x3/Ta thin film presents an increase in the Curie temperature, T_c , of about 68°C, as compared to Ta/NdFeBNbCu(540 nm)/Ta magnetic single layer.

4.3 Influence of Si addition

The addition of small amounts of Si to Nd-Fe-B system was reported to result in an increase in the Curie temperature, T_{cr} of the Nd₂Fe₁₄B phase, improvement of the intrinsic coercive field, H_{cr} of the nanocomposite magnets (Cui et al., 2000) and more rectangular hysteresis loops (Coey, 1996).

The influence of Nd-Fe-B-Nb-Cu film stratification and thermal treatments on the hard magnetic properties and microstructure of multilayer [NdFeBNbCu/FeBSi]xn thin films was recently studied (Chiriac et al., 2008). For multilayer [NdFeBNbCu/FeBSi]xn films, the thickness of Nd-Fe-B-Nb-Cu layers was varied from 30 to 540 nm and the thickness of the Fe-B-Si spacer layer was varied from 2.5 to 20 nm. The total thickness of Nd-Fe-B-Nb-Cu layers was 540 nm.

The composition of Fe-B-Si film obtained by SEM/EDS technique is as follows: Fe 70 at.%; Si 15 at.%; B up to 100 at.%.

During the annealing process, the elements within the Ta/[NdFeBNbCu/FeBSi]xn/Ta multilayer films diffuse and a mixture consisting of hard magnetic and soft magnetic phases is created in different ratios depending on the thicknesses of the constituent layers and annealing temperature. The X-ray diffraction investigations indicated that Ta/[NdFeBNbCu/FeBSi]xn/Ta thin films, in as-deposited state and after thermal treatments at temperatures below 570°C, have amorphous structure. At annealing temperatures between 570 and 600°C, the microstructure of the samples consists of a small number of Fe₃B nanograins, which are embedded in the amorphous matrix. Samples annealed at temperatures higher than 650°C exhibit a complex multiphase structure of tens of nanometers.

Figure 7 shows the X-ray diffraction patterns for selected samples in as-deposited state and after annealing at specific optimum temperatures as follows: Ta/NdFeBNbCu(540nm)/Ta single layer in as-deposited state, curve (a) and after annealing at temperature of 650°C for

20 minutes, curve (b), and multilayer Ta/[NdFeBNbCu(180nm)/FeBSi(15nm)]x3/Ta films after annealing at 680°C for 20 minutes, curve (c).



Fig. 7. X-ray diffraction patterns of the Ta/NdFeBNbCu(540nm)/Ta single layer in asdeposited state and after annealing at 650°C for 20 minutes (curves a and b), and multilayer Ta/[NdFeBNbCu(180nm)/FeBSi(15nm)]x3/Ta films after annealing at temperature of 680°C for 20 minutes (curve c).



Fig. 8. The dependence of the magnetic parameters on the thickness (t) of the Fe-B-Si layers for multilayer Ta/[NdFeBNbCu(180nm)/FeBSi(t)]x3/Ta films annealed at 680°C for 20 minutes.

It can be observed that the as-deposited Ta/NdFeBNbCu(540 nm)/Ta single layer has an amorphous structure. After annealing, the Ta/[NdFeBNbCu(180nm)/FeBSi(15nm)]x3/Ta multilayer film presents a multiphase structure consisting of a mixture of nanograins of

Nd₂Fe₁₄B hard magnetic phase and Fe₃B, Fe₂₃B₆, Fe₂B, FeSi, and Fe₅Si₃ soft magnetic phases (curve c). For the Ta/NdFeBNbCu/Ta single layer annealed at 650°C for 20 minutes, curve (b), the average crystalline size of Nd₂Fe₁₄B phase is about 35 nm, while for Ta/[NdFeBNbCu(180nm)/FeBSi(15nm)]x3/Ta multilayer film annealed at 680°C for 20 minutes, curve (c), is about 30 nm. The average crystalline size of soft magnetic phases is about 10 nm. In Figure 8, the dependence of the coercive field, H_c , saturation magnetization, M_{sr} , and remanent magnetization, M_{rr} , on the thickness (*t*) of the Fe-B-Si layers for Ta/[NdFeBNbCu(180nm)/FeBSi(15nm)]x3/Ta multilayer films annealed at 680°C for 20 minutes is presented.

It can be observed that the highest values of coercive field, saturation magnetization, and remanence are simultaneously reached when the thickness of the Fe-B-Si layers increases up to 15 nm. A decrease in coercive field and remanence was noticed when the thickness of Fe-Si-B layer was increased to 20 nm.

Typical magnetic hysteresis loops for Ta/[NdFeBNbCu(180nm)/FeBSi(15nm)]x3/Ta multilayer thin films annealed at different temperatures between 630 and 700°C for 20 minutes are shown in Figure 9.



Fig. 9. Room-temperature hysteresis loops of multilayer Ta/[NdFeBNbCu(180nm)/FeBSi (15 nm)]x3/Ta thin film annealed at different temperatures between 630 and 700°C.

It can be observed that the optimum magnetic parameters are obtained for the sample annealed at 680°C for 20 minutes. An obvious 'shoulder' on the hysteresis loops of the samples annealed at 630 and 650°C is observed, due to weak exchange coupling between the soft and hard phases.

In Figure 10, the hysteresis loops for Ta/NdFeBNbCu(540nm)/Ta single layer and Ta/[NdFeBNbCu(180nm)/FeBSi(15 nm)]x3/Ta thin film are comparatively presented.

One can observe that the stratification effect by using Fe-B-Si film as spacer layer has an influence on the rectangular aspect of the hysteresis loop of the Ta/[NdFeBNbCu(180nm)/FeBSi(15nm)]x3/Ta thin film as compared to the hysteresis loop of the Ta/NdFeBNbCu(540 nm)/Ta thin film.

The thermomagnetic measurements indicate that the Fe-B-Si spacer layer in multilayer Ta/[NdFeBNbCu(180nm)/FeBSi(t)]x3/Ta thin film results in an increase of the Curie

temperature. The thermomagnetic measurements for multilayer Ta/[NdFeBNbCu(180nm)/ FeBSi(15nm)]x3/Ta thin film annealed at 680°C for 20 minutes reveal an average increase in the Curie temperature of about 17°C, as compared to Ta/NdFeBNbCu(540nm)/Ta film.



Fig. 10. Room-temperature hysteresis loops of Ta/NdFeBNbCu(540 nm)/Ta single layer and multilayer Ta/[NdFeBNbCu(180nm)/FeBSi(15 nm)]x3/Ta thin film.

4.4 Influence of other additives

In Nd-Fe-B samples, the substitution of Nd by Dy increases the magnetocrystalline anisotropy of the Nd₂Fe₁₄B phase, giving rise to an improved coercive field without a significant loss in remanent magnetization (Kanekiyo and Hirosawa, 1998). By increasing Nd content from 14 to 20-30%, crystallization temperature of the hard phase decreases from 575° C to 500° C (Van Khoa et al., 2006).

The addition of 1.1 at. % Mo, Si or Ga to Nd-Fe-B system results in an increase in the Curie temperature, T_{cr} of the hard phases and the improvement of the intrinsic coercivity of the nanocomposite magnets (Cui et al., 2000).

Van Khoa and co-workers (2008) studied the effect of the thickness (d) of the Fe buffer layers on the Curie temperature and the remanent magnetization of the multilayer Si/Mo(20nm)/ [NdFeB(35nm)/Fe(d(Fe)](4)/Mo(30nm)(d(Fe) films. The Curie temperature and remanent magnetization of the films increased when thickness of Fe layer was increased from 0 to 10 nm and was decreased when thickness of Fe layer reached 15 nm.

The replacement of a Fe-based soft phase by a semihard phase (i.e. $Fe_{1-x}Co_x$ alloys) yields a trivial improvement of the coercive field because the average anisotropy (*K*1) increases. The $Fe_{1-x}Co_x$ alloys are ideal candidates for the hard-soft permanent magnet nanostructuring because they have a very high magnetization in a wide range of Fe-rich compositions, 24.3 kG in $Fe_{65}Co_{35}$ (Skomski et al., 2009; Ao et al., 2006).

Wang and co-workers (2007) show that the addition of Zr can prevent the formation of $Nd_3Fe_{62}B_{14}$ metastable phase and refine the grain sizes of α -Fe and $Nd_2Fe_{14}B$ phases, thus improving the magnetic properties, especially the coercive field of nanocomposite hard magnetic materials. The crystallization behavior changes from a two-step process to a
single-step process, and Nd₂Fe₁₄B and α -Fe precipitate simultaneously from the amorphous phase. The addition of Zr is also advantageous in improving the energy product and squareness of hysteresis loops in Nd₂Fe₁₄B/ α -Fe nanocomposites (Chang et al., 1999). Moreover, Jurczyk and Wallace (1986) reported that insertion of a proper amount of Zr in Nd₂Fe₁₄B phase may increase the anisotropy field of the alloy, and accordingly, H_c is remarkably increased, along with the magnetic energy product. The entrance of Zr element into Nd₂Fe₁₄B unit cell may slightly decrease the Curie temperature T_c of Nd₂Fe₁₄B phase.

5. Exchange coupling

It is well known that the good permanent magnetic properties of Nd-Fe-B nanocomposite magnets are generated through the magnetic hardening of the iron based soft magnetic phases (i.e. α -Fe, Fe₃B, Fe₂₃B₆) by the Nd₂Fe₁₄B hard magnetic phase. This occurs when the structure is homogeneous and refined to the nanometer scale, thus ensuring effective magnetic coupling of the grains over short distances through exchange interactions (Kneller and Hawing, 1991). Decreased grain size that leads to a stronger interface exchange coupling between grains (Cui and O'Shea 2003).

The appropriate refinement of the soft grains is favorable for the exchange fields from the nearest grains of the hard phase to fully cover the soft grain embedded between the hard grains and suppress the easy nucleation of inverse magnetization in the soft grain. On the other hand, the refinement of both the soft and hard grains results in a significantly increasing ratio of the interface area (or grain boundary area) to the volume of the grains. With an increasing percentage of grain interfaces or grain boundaries, the obstacles to propagation of inverse magnetization grow in number. Because the probability of the direct contact between the soft and the hard grains increases, the exchange coupling between the soft grain and the hard grains nearest in proximity is enhanced and plays an essential role in determining the magnetic properties of the nanocomposite magnets (Cui et al., 2000).

Exchange interactions between neighboring soft and hard grains lead to remanence enhancement of isotropically oriented grains in nanocrystalline composite magnets (Fidler and Schrefl, 2000). The magnetic properties of the samples decrease with the coarsening of the hard grains. The larger the hard grains the smaller probability of the direct contact between the soft and hard grains. Thus, for nanocomposite hard magnetic samples, the exchange coupling between the soft grain and its nearest hard grains is weakened. Thus, the magnetic properties of the nanocomposite magnets are deteriorated (Cui et al., 2000).

Too large or too small a grain size of α -Fe is unfavorable for the improvement of the magnetic properties of the nanocomposite hard magnetic samples. A α -Fe grain with a large grain size cannot be fully penetrated by the exchange fields coming from the hard magnetic grains nearest in proximity, due to the short-range feature of the exchange interaction. In this case, the nucleation of the reverse magnetization can be easily produced at the middle of the α -Fe grains, where it is free from the exchange fields. Obviously, this is harmful to the permanent magnetic properties. The too small α -Fe grains are always attained at a relatively low crystallization temperature at which the incomplete formation of the hard phase is obviously unfavorable for the magnetic properties of nanocomposite magnets (Cui et al., 2000).

The results obtained by Fukunaga and co-workers (1999) confirm the increase of coercivity owing to reduced intergrain exchange interactions, provided that grain size is sufficiently small. At the same time, small grain size of the hard phase facilitates the exchange coupling between grains, thus increasing the remanence. The authors proposed a two-phase microstructure consisting of Nd-Fe-B and α -Fe grains embedded within a residual amorphous phase. The amorphous intergranular phase is expected to reduce the exchange interactions between the hard and the soft grains, leading to an improved coercive field.

To obtain a more ideal structure with a uniform distribution of the soft and hard phases, a multilayered structure is a best appropriate way. Non-uniform clustering of α -Fe after annealing is not favorable for exchange coupling between the hard and soft phases, resulting in poor permanent-magnetic properties in the nanocomposite single layer (Liu et al., 2003).

The results concerning the magnetic interactions within the multilayer Ta/[NdFeBNbCu/FeBSi]x3/Ta thin films are presented in the following, based on some recent reports (Chiriac et al., 2008). The refinement of the grain sizes by a controlled thermal treatment was used to enhance the exchange coupling between the hard and soft magnetic grains in multilayer Ta/[NdFeBNbCu(180nm)/FeBSi(15nm)]x3/Ta thin films.

The δM versus H measurements are used to verify the nature of exchange coupling between the hard and soft magnetic phases in nanocomposite magnets. The δM is defined as $m_d(H)$ -[1-2 $m_r(H)$], where $m_d(H)$ is the reduced demagnetization remanence ($M_d(H)/M_r$) and $m_r(H)$ is the reduced magnetization remanence ($M_r(H)/M_r$) (Rama Rao et al., 2007). Figure 11 shows the δM plots for Ta/[NdFeBNbCu(180nm)/FeBSi(15nm)]x3/Ta thin films after annealing at different temperatures for 20 minutes.



Fig. 11. δM versus applied magnetic field for Ta/[NdFeBNbCu(180nm)/FeBSi(15nm)]x3/Ta thin films after annealing at different temperatures for 20 min.

It can be observed an increase in exchange interaction between the soft and hard magnetic grains with the increase of the annealing temperature to 680°C. For samples annealed at 630°C and 650°C an initially negative δM , for magnetic fields between 0 and about 6.8 kG, is observed, indicating the existence of magnetostatic interactions between soft and hard grains. A positive δM is observed afterwards indicating the existence of exchange coupling between soft and hard grains. For Ta/[NdFeBNbCu(180nm)/FeBSi(15nm)]x3/Ta thin film, annealing at a temperature increased to 680°C for 20 min., leads to a grain growth resulting in an effective exchange-coupling.

The strength of the coupling / decoupling of soft and hard magnetic grains is determined by variation of specific magnetization (σ) as a function of applied magnetic field (H). The irreversible susceptibilities χ_{irr} ($\chi_{irr} = d\sigma/dH$) as a function of the demagnetising fields for Ta/[NdFeBNbCu(180nm)/FeBSi(15nm)]x3/Ta thin films annealed at temperatures between 630°C and 680°C are presented in Figure 12. The main peaks correspond to the nucleation fields for magnetisation reversal. In comparison with the samples annealed at 680°C, for the samples annealed at 630°C and 650°C, non-simultaneous switching of the magnetization in the hard and soft magnetic phases leads to differences between the coercivity, H_{α} and the nucleation field, H_n .

The two peaks shown in the (χ_{irr}) curve of Figure 12 for the sample annealed at 630°C could be due to the presence of the smaller soft magnetic grains confirmed by an obvious shoulder in II quadrant of the hysteresis loop (Fig.9). From Figures 9 and 12 it can be observed that the Ta/[NdFeBNbCu(180nm)/FeBSi(15nm)]x3/Ta thin films annealed at 680°C for 20 minutes show a histeresis loop with no constriction and a strong exchange coupling effect between the soft and hard magnetic phases.



Fig. 12. The irreversible susceptibilities, χ_{irr} , as a function of the demagnetising fields for Ta/[NdFeBNbCu(180nm)/FeBSi(15nm)]x3/Ta thin films annealed at temperatures between 630 and 680°C.

6. Thermal stability

In order to be used in applications like MEMS devices, and information storage media, the thin film magnets should exhibit specific characteristics: (1) large coercivity, remanent magnetization, saturation magnetization (M_s) and energy product (BH)_{max}.; (2) good thermal stability; (3) adaptability to the specific applications processing. For permanent magnets that have to operate at elevated temperatures the irreversible loss of magnetization, which causes short-time or long-term flux losses, is an important criterion for evaluating the thermal stability (Liu and Davies, 2007).

The thermal stability of permanent magnets can be increased by increasing the Curie temperature and intrinsic coercivity. The increase of the Curie temperature, T_c , can be achieved by partial substitution of Fe with Co (Liu and Davies, 2007; b-Chiriac et al., 2007). Supplementary, as described in the previous chapter sections, the addition of elements like Nb or/and Cu, Mo and Zr to Nd(Fe,Co)B ternary films is an effective way to improve their hard magnetic properties.

The H_c and M_r losses (L) were calculated using following equations (Liu and Davies, 2007):

$$L_{H_c} = \frac{H_{cB}(25^{\circ}C) - H_{cA}(25^{\circ}C)}{H_{cB}(25^{\circ}C)} x100\%, \quad L_{M_r} = \frac{M_{rB}(25^{\circ}C) - M_{rA}(25^{\circ}C)}{M_{rB}(25^{\circ}C)} x100\%$$

where H_{cB} and M_{rB} , H_{cA} and M_{rA} are the room temperature coercivity and remanence, respectively, before (B) and after (A) exposure to an elevated temperature.

Nanocomposite alloys present irreversible losses lower than single phase nanocrystalline alloys, because of the additional exchange coupling and enhancement in M_r imparted by the presence of soft magnetic phase with a higher saturation magnetization than for the Nd₂Fe₁₄B hard phase (Liu and Davies, 2007).

Liu and Davies (2007) shown that the Co substitution improves the thermal stability of nanocrystalline (Nd/Pr)-(Fe/Co)-B alloys by reducing the long-term and short-time irreversible losses in coercive field and remanent magnetization as a result of the enhancement in Curie temperature and possibly also because of improved corrosion resistance. The thermal stability evolution of Nd-Fe-B, Nd-Fe-B-Nb-Cu and [NdFeBNbCu/Co]×3 thin films as a result of their thermal cycling in the temperature range 25÷350°C is comparatively presented.

The influence of the ageing at 150°C, for different periods of time, on the losses in H_c and M_r was also studied (Chiriac et al., 2009). All the as-deposited thin films were thermally treated in vacuum at 650°C for 20 min, for their devitrification and crystallization. In our experiments, the thermal stability of crystallized samples was estimated in two ways: (1) S1 sample sets were maintained at constant temperature (150°C) for different periods of time and the subsequent magnetic measurements were routinely performed after cooling at 25°C; (2) the magnetic characteristics of S2 sample sets were measured at different temperatures in the range 25÷350°C.

For the Ta/[NdFeBNbCu(540)/Ta thin film, the temperature coefficient of remanent magnetization (α) and the temperature coefficient of coercivity (β) in the temperature range 25°C÷150°C are – 0.029%/°C and –1.02%/°C, respectively.

Figure 13 shows the demagnetization curves for Ta/[NdFeBNbCu(180nm)/Co(2 nm)]x3/Ta thin film at various temperatures between 25°C and 350°C. It can be observed that the coercivity and remanence decrease with increasing the temperature up to 350°C, but they reach the initial value when cooling back to 25°C.

Based on the data presented in Figure 14, α and β coefficients in the temperature range 25°C÷150°C for Ta/[NdFeBNbCu(180 nm)/Co(2 nm)]x3/Ta thin film are about -0.025%/°C and -0.39%/°C, respectively. It can be observed that low values of the α and β coefficients for Ta/[NdFeBNbCu(180 nm)/Co(2 nm)]x3/Ta thin film in the temperature range 25°C÷150°C satisfy the needs of planar permanent magnets as actuator elements for MEMS applications (Walther et al., 2009).

The thermal stability of Ta/NdFeB/Ta, Ta/NdFeBNbCu/Ta and Ta/[NdFeBNbCu/Co]×n/Ta thin films represented by the losses in H_c and M_r has been also investigated. The Ta/NdFeB/Ta, Ta/NdFeBNbCu/Ta and Ta/[NdFeBNbCu/Co]×n/Ta thin-film magnets (sample set S1) were successively aged at 150°C for different time periods between 5 h and 500 h. For the samples aged for 100 h, the coercivity losses are of 0.8% for Ta/[NdFeBNbCu/Co]×3/Ta films, of 0.92% for Ta/[NdFeBNbCu/Ta films and of 1.1% for Ta/NdFeB/Ta films, whereas the remanence magnetization losses are 4.2%, 5.1% and 6.8%, respectively. The ageing of the Nd-Fe-B samples with additions at 150°C for time periods larger than 100 h, has not generated notable changes in coercivity and remanence losses.



Fig. 13. Demagnetization curves for Ta/[NdFeBNbCu(180nm)/Co(2nm)]x3/Ta thin films at various temperatures between 25° C and 350° C.

As compared to the samples aged at 150°C for 100 h, the Co-containing samples aged for 500 h exhibit changes in coercivity and remanence losses lower than 0.2% and 0.5%, respectively.

Figures 14.(a, b) present the evolution of the main magnetic parameters, coercivity (a) and remanence magnetization (b), of the sample set S2 as a function of temperature in the range 25÷150°C.

The results show that the coercivity losses increase with increasing the temperature, but they are reversible, which indicates that these thin films are suitable for high temperature applications.

In Figure 14 b, for all the samples, only small losses in M_r occurred for temperature up to 150°C, but afterwards the losses increase rapidly, especially for temperature higher than 200°C due to structural changes in the surface and volume of the samples after heating at high temperatures.

As compared to Ta/NdFeB(540)/Ta and Ta/[NdFeBNbCu(540nm)/Ta films, the Ta/[NdFeBNbCu(180nm)/Co(2nm)] \times 3/Ta films with a small Co content (about 1.5% in

total magnetic volume) exhibit H_c losses of about 26% and M_r losses of about 4%. This small change in the losses of Ta/[NdFeBNbCu(180)/Co(2)]×3/Ta samples is due to the increase in the corrosion resistance and in the Curie temperature with about 68°C.



Fig. 14. The evolution of the coercivity (a) and remanence magnetization (b) as a function of temperature for Ta/NdFeB/Ta, Ta/NdFeBNbCu/ and Ta/[NdFeBNbCu/Co]x3 films.

7. Conclusion

In nanocomposite magnetic materials, the ferromagnetic exchange interaction between the soft and Nd₂Fe₁₄B hard magnetic phases is largely influenced by the phase distribution, phase boundary conditions and grain size. Many attempts were made to improve the hard magnetic properties of nanocomposite permanent magnets.

In this chapter, a brief review on the influence of the additions such as, Nb and Cu, Co and Si, on the structure and hard magnetic properties of Nd-Fe-B nanocomposite thin films is presented, especially describing our recent results. Our results was mainly focused on the controlling the nanostructures by stratification of Nd-Fe-B-Nb-Cu magnetic layer and simultaneously addition of Co or Fe-Si-B as spacer layer.

For Nd-Fe-B thin films, the combined addition of Cu and Nb (Cu/Nb ratio of 1/3) in the Nd-Fe-B film and together with the use of the Co layers for stratification of the Nd-Fe-B-Nb-Cu layer are very effective tools for improving the coercivity and remanence values and for the increase of the Curie temperature. As compared to Ta/NdFeBNbCu(540nm)/Ta magnetic single layer, the multilayer Ta/[NdFeBNbCu(180nm)/Co(2nm)]x3/Ta thin film annealed at 650°C for 20 minutes exhibits very good hard magnetic properties such as coercivity of about 22.7 kOe and remanent magnetization of about 100.6 emu/g. The replacement of Fe by a small Co amount (about 1.5% from the total volume of multilayer [NdFeBNbCu(180nm)/Co(2nm)]x3 system) significantly increases the Curie temperature with about 68°C.

As a result of the stratification effect of Nd-Fe-B-Nb-Cu by using Fe-B-Si as spacer layer, the multilayer Ta/[NdFeBNbCu (180nm)/FeBSi(15nm)]x3/Ta thin film annealed at 680°C for 20 minutes exhibits very good hard magnetic properties such as: coercivity of about 22.8 kOe, saturation magnetisation of about 127.4 emu/g, remanent magnetisation of about 117.8 emu/g, an increase in Curie temperature of about 17°C, due to a strong exchange coupling between soft and hard magnetic phases. These samples present a more rectangular hysteresis loops.

We have demonstrated that, the directly inclusion in the Nd-Fe-B film volume of combined addition of Nb and Cu and stratification of Nd-Fe-B-Nb-Cu film by use of Co or Fe-Si-B film as spacer layer lead to the improvement of the hard magnetic properties of Nd-Fe-B films. A disadvantage of these samples regards the poor reproductibility of the magnetic properties since composite sputtering targets were used. Therefore, some of the future work within this topic will focus on the reproducibility of the magnetic properties by the use of the co-deposition from elemental targets.

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Novel Chemical Vapour Deposition Routes to Nanocomposite Thin Films

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1. Introduction

1.1 Nanocomposite thin films

Thin films containing nanoparticles are of interest to a wide variety of industries including but not limited to: electronics, sensing, glazing, catalysis, semiconductor and computing. The interest from these industries arises from the wide variety of properties that such composite thin films can display such as: optical, catalytic, electrical and thermal conductivity, antibacterial, Chromeogenic, photoluminescence, sorbents, plasmon resonance and colour (Green 2005; Jain et al. 2007; Walters & Parkin 2009b). Much information has been published on the synthesis of nanoparticles and ways to control their size and shape, hence properties. Much less has been written on the incorporation of such nanoparticles into composite thin films, which can then be used in useful devices.

1.2 Current routes to nanocomposite thin films

Current approaches to nanocomposite thin films such as sol gel routes require one or more distinct steps. These are outlined below in figure 1.

Route 1 involves the synthesis of the semiconductor matrix followed by the addition of nanoparticles in a second step. Examples of this technique include sol-gel methodologies such as spin coating or dip coating (Hida & Kozuka 2005; Yang et al. 2005).

Route 2 is similar to route 1 in that the semiconductor matrix is first constructed and the nanoparticles are formed within the film from metal ions added by a process such as highenergy ion implantation or use of a metal solution followed by heat treatment or catalytic reduction (Tzu-Hsuan & et al. 2006; Wang et al. 2006).

Route 3 is the synthesis of both nanoparticles and semiconductor matrix in a single step, for example by multi target magnetron sputtering or dual source chemical vapor deposition. Sol-gel techniques where both nanoparticle and semiconductor precursors are used has also been investigated. Liquid phase deposition has also received some attention (Houng & Huang 2006; Ko et al. 2005; Liao et al. 2006; Silva & Nicholls 2001).

Route 4 is the layer-by-layer deposition of metal particles and semiconductor material by a methodology such as multiple target laser ablation or pulsed laser deposition (Frey et al. 2006; Gyorgy et al. 2006; Serna & et al. 2006; Zorica & et al. 2006).

In routes 2-4 nanoparticles are formed in situ or concurrently with the semiconductor matrix, this significantly limits the type of nanoparticle that can be incorporated. The use of

preformed nanoparticles as in route 1 is highly desirable as a much wider range of nanoparticles can be used.



Fig. 1. Routes to nanocomposite thin films. (Palgrave and Parkin 2006)

In this chapter we will outline several different CVD approaches that allow for the deposition of nanoparticle / semiconductor composite thin films in a single step – route 5 in figure 1. The methodologies are based on the incorporation of an aerosol into the process, essentially the use of a liquid-gas aerosol to transport precursors to a heated substrate. Traditionally this approach has been taken where a conventional CVD precursor proves to be thermally unstable or involatile (Hitchman & Jensen 1993). A much wider range of precursors are available when using an aerosol delivery system. For example, exotic species such as ionic salts and metal oxide clusters have been used to deposit thin films in aerosol processes (Binions et al. 2004; Cross & Parkin 2003).

We will describe the use of colloidal suspensions as precursors towards nanocomposite thin films. In many ways colloidal suspensions are the antithesis of a CVD precursor, which normally requires volatile molecular species. The use of an aerosol allows for the transport of preformed nanoparticles, these may be incorporated into a conventional CVD flow (hybrid CVD) or transported with another semiconductor precursor (aerosol assisted CVD or AACVD)

There are three main benefits to these techniques over others. First, they are flexible: many preformed nanoparticle solutions can be used, and combined with any chemically compatible precursor, to produce a large range of nanocomposite films. Second, CVD is a widely used industrial technique in fields such as microelectronics and glazing, and it has a number of well-known advantages, not least the deposition of adherent, conformal films. Thirdly these techniques are relatively simple one step processes that do not require ageing times or special handling steps.

1.3 Chemical vapour deposition

All CVD processes have a number of common steps (illustrated in figure 2) these are:

- 1. Precursor, generation of active gaseous reactant species.
- 2. Transport, delivering the precursor into the reaction chamber.
- 3. Adsorption of the precursor onto the hot surface.
- 4. Decomposition of the precursor to give the atom needed for the film and organic waste.
- 5. Migration of atoms to a strong binding site.
- 6. Nucleation that leads to the growth of the thin film.
- 7. Desorption of unwanted side products.
- 8. Removal of unwanted products.



Fig. 2. Diagram to show the pathway of CVD reactions adapted from (Hitchman & Jensen 1993).

1.3.1 Precursor, generation of active gaseous reactant species.

The selection of a suitable precursor is essential for the process. For traditional CVD processes the precursor must be highly volatile in order to ensure enough partial pressure so that it can easily be promoted into the gas phase. If the precursor is a liquid or a powder this can be achieved using a heated bubbler. The precursor must also be stable in the bubbler and during gas phase transport only reacting with the heated substrate. As with all chemical synthesis it is desirable for the precursor to be readily available at high purity and at a reasonable price.

1.3.2 Transport, delivering the precursor into the reaction chamber.

Delivery is via an inert carrier gas (e.g. N_2 (Kuroda et al. 1989)or Ar), a reactive gas (e.g. O_2 (Miao et al. 2005) or H_2) or a mixture of the two. Inert carrier gases are the most commonly used as they transport the precursor into the reaction chamber without significantly affecting the properties of the deposited film. Oxygen can be used as a reactive carrier gas to oxidise the precursor to form a metal oxide thin film. Using a mixture of oxygen and

nitrogen, the stoichiometry of the metal oxide formed can be controlled by changing the concentration of the gases. There have also been complex examples using mixtures of reactive carrier gases such as (e.g. Ar-N₂-BF₃-H₂) (Zhang et al. 2002)

1.3.3 Adsorption of the precursor onto the hot substrate.

The hot surface required for CVD is essential to overcome the energy barrier of reaction. Both hot and cold wall reactors can be used. A cold wall CVD reactor is where the substrate is the only piece of apparatus heated and deposition occurs only on the substrate. However, in hot wall CVD the entire reactor is heated. This clearly means the deposition can occur on the walls as well as the substrate, which can result in wastage of precursor. However, it also ensures that the heat distribution across the substrate is completely even helping to deposit a more consistent film. The use of a hot wall reactor also mitigates the affects of thermophoresis. Thermophoresis is a phenomenon where particles (such as aerosol droplets) experience a force in the direction of a temperature gradient, this is where they are directed away from the heated substrate leading to a less adhesive film (Hampden-Smith & Kodas 1999).

1.3.4 Decomposition and reaction of the precursor.

The decomposition of the precursor can occur in the gas phase or on the substrate surface. If reaction happens in the gaseous phase the precursor may "snow" onto the surface creating a weaker and lower density film. If this occurs there are also other problems that can occur such as pin hole defects in the film surface. In some cases the gas phase reaction can be fundamental to the film growth mechanism, e.g. a gas phase adduct in the formation of Tantalum phosphide (Blackman et al. 2003) If however the dissociation of the intermediate does not occur until in contact with the surface, the material required for a film; often a metal, or metal oxide, separates itself from the organic part, e.g. the formation of a WO₃ thin film from WCl₆ with O containing reactive solvents (Blackman & Parkin 2005).

1.3.5 Migration of atoms to a strong binding site.

This is where a chemical reaction with the surface takes place changing the process from physisorption to chemisorption. The surface species target an activated site e.g. a defect site or step site where the energy needed to bind is lower.

1.3.6 Nucleation leading to film growth.



Fig. 3. Diagram to show different growth mechanisms within CVD adapted from (Binions 2009).

There are three main types of film growth mechanisms in CVD (Figure 3.). The determining factor by which the growth occurs is due to the affinity of the precursor to the substrate and the precursor flux to the substrate. If the bond formed between the precursor and the substrate is stronger then layer-by-layer growth is more likely. If however the precursor-to-precursor bond is stronger island growth occurs. Stranski-Kastanov(Michael L. Hitchman 1993) growth occurs when both growth types occur either layer growth followed by island growth, or island growth followed by layer growth.

1.4 Chemical vapour deposition for nanocomposites 1.4.1 Plasma enhanced chemical vapour deposition

Plasma enhanced chemical vapour deposition (PECVD) can be characterised as when a plasma, created by an intense electric field, is used to activate precursor species before they reach the surface of the substrate. This high intensity field interacts with gaseous electrons

and accelerates them; this causes the electrons to collide with precursor species and potentially ionise them. The field also interacts with ions but because of the larger mass of these, has a significantly lesser effect.

PECVD has been used in two distinct ways to synthesise nanocomposite materials. The first of which is to coat commercially purchased titanium dioxide nanoparticles that were then attached to a silicon wafer substrate. Polymeric coatings were produced from a variety of different plasmas, the most useful of which was HMDSO (hexylmethyldisiloxane) and O₂. The coatings were conformal and enabled coated nanoparticles to stay dispersed in solution for longer periods of time (Shearer et al. 2010).

PECVD has also been used to prepare diamond like carbon (DLC) thin films that have also been grown containing nanoparticles, notably gold or titanium oxides. DLC and the nanoparticles are found using electron microscopy to deposit as segregated phases. This allows the size of the nanoparticulate agglomerate to control properties such as surface roughness and hydrophilicity in the case of titanium dioxide and film colour in the case of gold. The use of gold nanoparticles in these composites leads to the observation of a surface plasmon resonance (SPR) in the UV/visible spectrum. It was found that the SPR centre could be controlled by careful consideration of the gold concentration in the gas phase. A higher proportion of gold led to larger gold nanoparticle agglomerates and a subsequent red shift in the colour of the film from 550 nm to 570 nm (Paul et al. 2009).

1.4.2 Direct liquid injection

Direct liquid injection (DLI) is a relatively new development in precursor deployment where a liquid phase precursor is introduced into the CVD reactor system in a systematic and controlled manner, often involving flash evaporation of the liquid precursor in the gas stream, a schematic of the setup is depicted in figure 4. DLI CVD has had limited use in the production of nanocomposite thin films; only having been used to introduce metal nanoparticles into thin films of TiO_2 with a view to producing antibacterial films.

Maury et al. grew nanocomposite thin films of TiO_2 containing copper nanoparticles using titanium tetraisopropoxide (TTIP) and copper bis (2,2,6,6-tetramethyl-3,5-heptadionate), Cu (THMD)₂, as organometallics precursors. Liquid solutions of the precursors were prepared in xylene and were injected into the CVD reactor system via a flash evaporation chamber. Nanocomposite thin films were deposited at 683 K on glass, silicon and steel substrates. Electron microscopy revealed that the copper was incorporated as metal particles with diameters between 20 and 400 nm. The authors note that the incorporation of larger

fractions of copper nanoparticles led to a higher anatase content in the TiO_2 matrix and a higher antibacterial activity (Mungkalasiri et al. 2009).



Fig. 4. Schematic of the direct liquid injection chemical vapour deposition system adapted from (Mungkalasiri et al. 2009).

The same group examined the production of nanocomposite thin films of TiO_2 containing silver nanoparticles grown from TTIP and silver pivalate using the same experimental setup. Silver nanoparticles were observed during transition electron microscopy with a diameter range of 5 – 10 nm, somewhat smaller than comparable nanocomposite produced by sol-gel methodologies [ref]. The films were found to be bactericidal with an Ag/Ti ratio of 0.15 and above. The films were also investigated for their photocatalytic activity and compared with a plain TiO₂ film grown under the same conditions. The incorporation of silver nanoparticles into the matrix reduced the photocatalytic activity of the nanocomposite thin films compared to the plain film and higher doping levels (Ag/Ti > 0.1) leads to photocatalytic inactivation (Mungkalasiri et al. 2010; Page et al. 2007).

1.4.3 Atmospheric pressure chemical vapour deposition

Atmospheric pressure ahemical vapour deposition (APCVD) has been used to investigate the production of thermochromic nanocomposite thin films by Parkin et al. in a series of papers investigating the dual deposition of VO₂ and TiO₂ or SnO₂ (Manning et al. 2005; Qureshi et al. 2006; Qureshi et al. 2004).

Vanadium dioxide films were synthesised from the atmospheric pressure chemical vapour deposition reaction of vanadium oxychloride (VOCl₃) or vanadium tetrachloride (VCl₄) and water. The formation of a nanocomposite thin film was achieved by codeposition with

another metal oxide precursor that reacted at a faster rate than the vanadium precursor, $SnCl_4$ and $Ti(OPr)_4$ were utilised for this purpose (Manning et al. 2005).

The titanium dioxide and vanadium dioxide nanocomposites were formed from the codeposition of VCl₄ and Ti(OⁱPr)₄ at 650 °C. The nanocomposite thin films contained two major crystal morphologies on inspection by scanning electron microscopy, the first, rectangular like deposits of vanadium dioxide 3 μ m x 200 nm in size, the second approximately spherical deposits of titanium dioxide of varying diameters. The films were found to have both thermochromic properties, with a metal semiconductor transition occuring at 54 °C and photcatalytic properties, albeit with activity at a 10% level of a plain anatase titanium dioxide film used for comparative purposes (Qureshi et al. 2006).

Tin dioxide and vanadium dioxide thin films were preared from the codeposition of $SnCl_4$ and VCl_4 at 625 °C. The films had a morphology of 50 nm particles aggregated into larger islands some 200 nm in diameter. Energy dispersive analysis of X-rays (EDAX) indicated that tin was present throughout the films, but that vanadium was present in only trace, a few atomic percent, levels (Qureshi et al. 2004).

The authors advance the theory in this paper that nanocomposites are formed rather than solid solutions when both metal precursors have fast gas phase reaction rates. In this instance the oxygen precursor (water in this case) is used up much more quickly to generate segregated metal oxide islands on the substrate surface and a nanocomposite is observed with segregated oxide phases. In the alternative example, where there is a significant difference between metal precursor gas phase reaction rates e.g. VCl₄ and WCl₆ a solid solution of the less reactive precursor metal is formed in a metal oxide film of the more reactive precursor, $V_{1-x}W_x$ O₂, as molecules of the less reactive metal precursor become trapped in the growing metal oxide film and become incorporsted into the crystal structure.

2. Aerosol assisted chemical vapour deposition of nanocomposite thin films

2.1 Introduction to AACVD

Aerosol assisted chemical vapour deposition (AACVD) is based on a liquid – gas aerosol to transport soluble precursors to a heated substrate. The method has traditionally used where conventional CVD techniques have proved inadequate; for example when an APCVD precursor is involatile or thermally unstable (Hitchman & Jensen 1993). The requirements of precursors for AACVD are somewhat different than those for other CVD techniques; the restrictions of volatility and thermal stability are removed. Indeed the most important consideration for AACVD precursors is solubility, which allows a wide variety of unusual precursor systems and materials to be investigated including metal oxide clusters and ionic thin films (Binions et al. 2004; Cross & Parkin 2003).

The AACVD system has several advantages compared to other systems. Firstly it is enormously flexible. A wide variety of precursor solutions can be used; changing the content of the precursor flask can control film doping and a wide variety of solvents can be utilised (Parkin et al. 2008). Further to this precursor solutions may contain preformed nanoparticles or nanoparticle suspensions that can be deposited along with any chemically compatible precursor to produce a wide range of nanocomposite thin films. Secondly, CVD is a widely used industrial technique in fields such as microelectronics and window coating and has a number of well-known characteristics such as the production of adherent and conformal films (Jones & Hitchman 2009). AACVD has the potential to be inexpensively incorporated into current processes for the production of thin film nanocomposites.



Fig. 5. Schematic (Left) and photograph (Right) of the AACVD system.

The typical AACVD set up involves five key parts (as shown in figure 5). The system must contain a carrier gas; typically this is an inert gas such as nitrogen or argon although a reactive gas such as oxygen could be used. Second, the system must contain a precursor source such as a flask with precursor inside. Third, a method of generating an aerosol of the precursor solution and carrier gas, this can be done by forced wave ejection using a humidifier, atomisation using a spray nozzle or similar. Fourth, a method of controlling the temperature of the system and finally a reaction chamber, which may be hot or cold wall depending on the precursor system to be used, the size of the aerosol particles and the desirability or otherwise of thermophoretic effects.

Several key variables can be controlled in AACVD, these are; carrier gas flow rate. Controlling the flux of solvent and precursor to the substrate can have pronounced affects on not just the flow conditions (laminar versus turbulent) but also on the surface chemistry and precursor decomposition pathways and subsequent incorporation of impurities into the film. Precursor flask composition is important in controlling the final film composition; in AACVD a simple change in the ratio of precursors in the flask has proven to be a reliable way to control deposited film composition. The substrate temperature may be controlled and as in any CVD reaction is important for determining the surface chemistry and film growth energetics. It is also important along with aerosol particle size, which can be controlled by changing nozzle or humidifier operating frequency, in suppressing or encouraging thermophoresis. (Piccirillo et al 2008)

2.2 AACVD of nanocomposite thin films

AACVD has been used for the production of nanocomposite thin films since 2006 (Palgrave & Parkin 2006). Palgrave et al. described the production of nanocomposite thin films of titanium or tungsten oxides encompassing gold nanoparticles. This was the first example of a thin film nanocomposite being grown using AACVD from a preformed nanoparticle solution. The ratio of gold precursor to metal precursor in the precursor flask was demonstrated to control the final film composition. The addition of gold nanoparticles into the films led to the observation of a surface plasmon resonance band in the UV/Vis spectra. In the same year Gleason et al. combined ultrasonic atomization and plasma enhanced CVD to produce nanocomposites of silicon dioxide and dextran.

The deposition of Cr_2O_3 based nanocomposites incorporating fullerene like tungsten disulfide nanoparticles for the production of wear resistant thin films was studied by Choy

et al. The authors demonstrate the facile production of nanocomposite thin films using this method and report that the coefficient of friction of the films is reduced by some 30% on the incorporation of the nanoparticles. The film contact angle was significantly changed from hydrophilic (8°) for plain Cr_2O_3 to hydrophobic (105°) for the nanocomposite thin film (Choy & Hou 2008; Ross and Gleason 2008).

AACVD has been demonstrated by Quershi et al. to transport and deposit nanoparticulate powders as long as they could be adequately dispersed in solution. The use of "aerosol assisted deposition" allowed for a thin film of WO_3 to be synthesised from a dispersion of WO_3 nanoparticles in toluene. The films were deposited alongside TTIP in order to make a titanium dioxide and tungsten trioxide nanocomposite thin film. The films were found to have an unusual crenulated morphology that was not possible to recreate using other techniques such as sol-gel or APCVD. The presence of WO_3 could not be detected using X-ray diffraction or Raman and the films retained both photocatalytic ability and hydrophobicity (Qureshi et al. 2007).

Qureshi et al. have also examined the deposition of titanium dioxide and titanium dioxide nanocomposites using AACVD (Qureshi et al. 2009). TTIP was used as a titanium precursor and dissolved in toluene, whilst a commercially sourced cerium dioxide nanopowder aqueous suspension was used to deposit cerium dioxide. The two precursors were deposited alternately to form layers of titanium dioxide and cerium dioxide on glass substrates. The resulting films consisted of islands of titanium dioxide approximately 150 nm in diameter covered in cerium dioxide nanoparticles between 10 and 15 nm in diameter (Figure 6).



Fig. 6. (Left) SEM image showing a compact background with nanoparticles of approximate diameter 12 nm along with larger ovals 100 nm wide. (Right) Decrease in stearic acid C-H peak area for a ceria-titania film prepared by AACVD at 500 °C upon radiation with UV light (Qureshi et al. 2009).

The nanocomposite thin film showed promise both for photocatalysis (Figure 6) and as a super hydrophilic coating, although no significant increase in photocatalytic ability or reduction in contact angle of the composite film was reported compared to a plain titanium dioxide anatase thin film.

Walters et al. in their 2009 paper investigated the use of p-type dopants and noble metal dopants to influence the preferential orientation of ZnO thin films (Walters & Parkin 2009a). Films were prepared using AACVD from zinc acetylacetonate in water with one of the following as a nanoparticle source; auric acid, silver acetylacetonate, copper (II) acetyl acetonate or aluminium nitrate. The choice of nanoparticle precursor fundamentally changed the morphology of the deposited nanocomposite film (figure 7).



Fig. 7. SEM morphology of Ag Doped ZnO thin film Al (Al₂O₃) doped ZnO thin Film (400° C) of Cu (CuO/Cu₂O) doped ZnO thin films (Walters & Parkin 2009a).



Fig. 7D. Comparison of XRD pattern for Al doped ZnO thin film and Undoped ZnO thin film c) XRD pattern for ZnO Au and Ag doped thin films (Walters & Parkin 2009a).

The authors report that the incorporation of aluminium oxide and copper oxide nanoparticles was much easier and likely to be due to the reaction of the copper and aluminium precursors on the surface of the growing film. In contrast the incorporation of gold and silver nanoparticles was difficult due to thermophoretic effects this suggests that nanoparticle formation of these materials occurs primarily in the gas phase. This is unsurprising as silver and gold are poorly oxophillic and thus are more inclined to form metal nanoparticles rather than bonding to surface oxygen sites on the growing film.

The incorporation of nanoparticles into the zinc oxide films led to significant changes in the preferred orientation of the deposited films (figure 7D). As deposited zinc oxide films showed a preference for a (002) orientation that has been reported as the most electrically conductive for zinc oxide, the incorporation of Al_2O_3 , Au or Ag nanoparticles saw the preferred orientation change to the (101) direction, whilst the incorporation of copper appeared not to affect the film orientation.

Most recently Warwick et al. have investigated the use of AACVD for the production of multifunctional thin films. The authors deposited nanocomposite thin films where both the host matrix and guest nanoparticles had independent and well-established functional properties. Photocatalytic titanium dioxide was chosen for the host matrix and tin oxide for the guest nanoparticles. Tin oxide is well known for being infrared reflective and finds use in Low emissivity glazing (Warwick et al. 2010).

Precursor flasks were prepared with constant amounts of tin dioxide nanoparticles dispersed in methanol and varying levels of TTIP as the titanium precursor and varying levels of tin dioxide nanoparticles dispersed in methanol (Table 1). Scanning electron microscopy (figure 8.) indicated an island growth morphology. A typical island size of 300 nm and significant island agglomeration is observed for titanium dioxide films grown without any nanoparticles (figure 8A).

The incorporation of tin dioxide nanoparticles into the films (figure 8B & 8C) did not change the island size but affected the agglomerate size. As more nanoparticles were incorporated the agglomerate size increased from 400 nm for sample 4 (0.8 at. %. nanoparticles) to 1,200 nm for sample 2 (Figure 8C, 3.0 at. %. nanoparticles).



Fig. 8. Scanning electron microscope images of nanocomposite samples: A) TiO_2 , B) TiO_2 containing 1.8% SnO_2 nanoparticles and C) TiO_2 containing 3.0% SnO_2 nanoparticles (Warwick et al. 2010).

Analysis with energy dispersive analysis of X-rays indicated that the films contained titanium, oxygen and tin (summarised in Table 1.) and no contaminant. X-ray photoelectron spectroscopy confirmed the presence of tin dioxide nanoparticles throughout the thickness of the nanocomposite film.

Sample	Volume of 0.05M Ti(ⁱ OPr) ₄ solution in reaction flask / ml	Volume of SnO ₂ nano- particle solution in reaction flask / ml	Phase as determined by EDAX/XRD [film thickness / nm]	Sn concentration as determined by EDAX & WDAX / at. %.
1	1	0 (25 ml of Toluene used)	Anatase TiO ₂ [1050]	0
2	1	25	Anatase TiO ₂ [980]	3.0
3	2	25	Anatase TiO ₂ [990]	1.8
4	3	25	Anatase TiO ₂ [1085]	0.9
5	4	25	Anatase TiO ₂ [915]	0.8

Table 1. Table of experimental conditions and analytical results. All depositions were performed with a substrate temperature of 450 °C and a carrier gas flow rate of 1 l.min⁻¹.

Photocatalysis is the primary functionality of the titanium dioxide film and methylene blue testing was carried out to gain information on the relative photo-catalytic abilities of the films. A plain titanium dioxide film performed the best and the inclusion of tin dioxide nanoparticles led to a minimal decrease in photo-catalytic ability, and not appear to correlate with the percentage of nanoparticles incorporated into the film. The reflectivity in the near infrared region (1500 – 2500 nm) was investigated using UV/Vis. The authors report that the reflectance of the films in this region increased with the incorporated in dioxide nanoparticles. This correlated with the percentage of nanoparticles incorporated in the film, with higher nanoparticle incorporation leading to higher infrared reflectance (Figure 9). The inclusion of 3 at. % tin oxide nanoparticles caused a lower of reflectance at 2000 nm of 26 %. A plain titanium dioxide film showed a reflectance at 2000 nm of 17 %.



Fig. 9. Far infrared reflectance spectra of titanium dioxide tin dioxide nanocomposites (Warwick et al. 2010).

3. Hybrid chemical vapour deposition

3.1 Introduction to hybrid CVD

Hybrid CVD combines atmospheric pressure CVD and aerosol assisted CVD. The technique was first developed by Binions (Binions 2009) as a method of combining unusual precursor species in a more traditional CVD setup whilst avoiding the potential pitfalls of aerosol based systems. AACVD is advantageous in that it allows the use of exotic precursor species, such as nanoparticle dispersions, but does not guarantee that adherent thin films will be produced from them. Indeed it has been observed in several papers that the use of certain precursors in AACVD leads to powdery and poorly adherent films (Binions et al. 2004).

A schematic setup of the hybrid CVD system is shown below in figure 10. The system combines a conventional APCVD setup with an aerosol inlet into the reaction chamber.

The first setup used by Binions added the aerosol mist into the plain line flow and this had to pass through the mixing chamber. This tended to cause blockages, as the APCVD precursors would often readily react with the aerosol solvent, leading to the deposition of metal oxide in the mixing chamber. The positioning of the aerosol inlet relative to the APCVD inlet has also proven to be crucial to obtaining good quality films. For the best quality films the aerosol inlet needs to be directly underneath the APCVD inlet, this ensures good mixing of the two flows, even distribution of nanoparticles through out the deposited film and a suppression of thermophoretic effects. If the inlet is placed in another position then thermophoresis of the aerosol droplets can be a problem and as a consequence there is poor distribution of nanoparticles in the resultant film and significant deposition on the reactor top plate rather than the desired substrate.



Fig. 10. Schematic of hybrid aerosol assisted and atmospheric pressure chemical vapour deposition rig (Binions 2009).

3.2 Hybrid CVD of nanocomposites

Hybrid CVD has been used to deposit a variety of thermochromic nanocomposite thin films in an effort to improve the potential energy saving affect that a thermochromic coating may have in an intelligent glazing system. Thermochromic thin films (figure 11) have been postulated as useful in glazing for some time (Binions & Kanu 2010) as above a certain (tuneable) temperature the film becomes reflective to incoming infrared solar radiation reducing the amount of solar heat gain in the building and reducing the need for air conditioning. At lower temperatures solar heat gain is maximised and there is less need for heating.



Fig. 11. Schematic of the application of thermochromic materials to advanced window glazing

Current approaches use static systems, with invariant properties, such as always infrared reflective. However, such systems are less suitable for variable climates such as those found in the UK or USA as they either minimise solar heat gain causing a need for extra heating in winter or maximise solar heat gain causing a need for extra cooling in summer. Thermochromic coatings theoretically maximise heat gain in winter and minimise heat gain in summer. Currently thermochromic thin films are not commercially available.

Composite VO₂ / Au nanoparticle films were grown by the use of hybrid aerosol assisted / atmospheric pressure CVD from [HAuCl₄] and tetraoctylammonium bromide (TOAB) in methanol (the aerosol component) and [VO(acac)2] (the atmospheric pressure component). The films showed good surface coverage, uniformity and reproducibility. Increasing or decreasing the time of deposition could easily vary film thickness. In all cases at least the first 75% of the substrate is covered, similar to that observed previously with VO₂ films produced from the APCVD reaction of vanadyl acetylacetonate and with other APCVD systems. Similarly there are changes in thickness that correlate with the temperature gradient across the substrate surface as seen previously (Binions et al. 2007) and a highly uniform area 2 cm x 5 cm in the middle of the substrate.

Secondary electron imaging (Figure 12A) indicates the formation of rod like crystallites of VO₂ around 100 nm in width and up to 1.5 μ m long on the surface of the substrate, similar to morphologies previously seen in samples from the APCVD reaction of vanadyl acetylacetonate (Binions et al. 2007). Backscattered electron images (Figure 12B) indicate that gold is widely dispersed amongst the crystallites on the surface, rather than segregating as independent gold crystallites as has been observed with other methodologies, notably sol gel (Béteille et al. 1997).



Fig. 12. A) Secondary electron image and B) Back scattered electron image of a sample typical of these gold doped vanadium dioxide sample deposited using the combined system over 15 minutes at a temperature of 525 °C (Binions et al. 2008)

Analysis with energy dispersive analysis of X-rays indicated that the films contained vanadium and gold and no contaminant, at least to the limit of detection of the EDAX methodology (around ¹/₂ atom % depending on the element). The amount of gold in the film was proportional to the ratio of the precursor flows.

In some circumstances TOAB was added to the reaction mixture in order to improve the particle size distribution. Scanning electron microscopy (Figure 13.) of these films indicated an island growth morphology. Typically for samples produced with TOAB a smaller average island size of 75 nm (Figure 13A) is seen compared with 150 nm (Figure 13B) for those produced without.



Fig. 13. Secondary electron scanning electron microscopy pictures of typical samples of a VO_2 / Au nanoparticle film produced using the hybrid AA/AP CVD methodology grown (A) with TOAB (B) without TOAB (Saeli et al. 2009a).

Backscattered electron imaging of films produced with TOAB and EDAX spot analysis indicated that gold is found amongst the crystallites on the surface. There were stark

differences between the gold crystallites grown with TOAB (Figure 14A) and those grown without (Figure 14B). The gold crystallites in films grown with TOAB formed spherical agglomerates with a diameter in the region of 70 ± 10 nm. The gold crystallites in films grown without TOAB were very different; the crystallite agglomerates were smaller, around 40 nm diameter, and highly interconnected with no particular shape.



Fig. 14. Back scattered secondary electron scanning electron microscopy of typical samples of a VO_2 / Au nanoparticle film produced using the hybrid AA/AP CVD methodology grown (A) with TOAB (B) without TOAB (Saeli et al. 2009a).

The microstructure of the films is significantly altered due to the use of TOAB in the reaction; in depositions without TOAB the island size of vanadium dioxide particles is around 150 nm and there is significant interconnectivity between agglomerates (Figure 13B), similar to that previously seen, whilst with the use of TOAB the agglomerate size is reduced to 75 nm and leads to a more discreet, rounded morphology. A similar effect is seen when observing the gold nanoparticles in the films using backscattered electron imaging (Figure 14.). The films produced without TOAB show a variety of gold nanoparticle shapes and sizes, significant but random agglomeration and interconnectivity. The films produced using TOAB are very different, the gold nanoparticle agglomerates are uniform in shape and size (approximately 75 nm diameter spheres). This is due to a surfactant effect caused by the TOAB that has been seen previously (Saeli et al. 2009b). It is less expected that the use of TOAB would cause a change in the overall film morphology between films grown under otherwise identical conditions.

The colour of the films could be altered substantially with a range of blues and greens being produced in contrast to the yellow/brown colour normally associated with monoclinic vanadium dioxide; this is attributed to the inclusion of gold nano-particles in the VO₂ matrix. UV/Vis absorbance spectroscopy of the gold doped films indicates that a plasmon resonance band is present; however this is very broad, ~100 nm, due to significant variation of gold nano-particle size (Figure 15.). The strength of the band correlates strongly with the gold to vanadium ratio in the films. The addition of TOAB into the precursor flask also causes a significant shift in the SPR centre as the size of the nanoparticles becomes more clearly defined (Figure 15).



Fig. 15. UV/Vis spectroscopy and surface plasmon centres of typical samples of a VO₂ / Au nanoparticle film produced using the hybrid AA/AP CVD methodology grown with TOAB and without TOAB. The arrows mark the position of the surface plasmon band resonance centre. The absorbance spectrum of a VO₂ film is included for comparison (Saeli et al. 2009a).

X-ray diffraction analysis (Figure 16) indicated that in all cases cubic gold and monoclinic vanadium dioxide are formed. In some cases there is some evidence of the formation of V_2O_5 . This is not entirely unexpected as X-ray photoelectron analysis of the sample surface suggests a variety of vanadium environments, we believe V_2O_5 to be present only at the surface; indeed, on etching only a single vanadium environment is observed consistent with vanadium dioxide. Previous work on vanadium dioxide by APCVD has seen a similar phenomenon and has shown that surface V_2O_5 does not affect the thermochromic behaviour of the bulk film(Binions et al. 2007). XPS shows that the gold is found in a single metallic environment, this indicates several things: There are no other detectable gold compounds present in the film, there is no un-reacted precursor on the film surface and indicates that the gold is present only as gold nanoparticles on the surface and in the bulk of the host film matrix. XPS and Raman spectroscopy were used to evaluate carbon contamination in the films; carbon could not be detected in the bulk of the films using these methods, some carbon was detected on the surface of the films using XPS but is most likely from an external source.

All of the films show thermochromic behaviour with reduced transition temperatures. Typically the hysteresis width of gold doped vanadium dioxide thin films is quite wide in the range of 15 – 20 °C compared to 10 °C as seen with some tungsten doped samples produced by APCVD and 10 – 15 °C seen for films produced by Sol-Gel methodology (Béteille & Livage 1998). The hysteresis width seemed not to matter on the amount of gold present in the film. Ideally this hysteresis would be as thin as possible to maximise the energy saving effect. The hysteresis width is attributable to several factors such as a variety of grain size and or crystallographic orientation (Binions et al. 2007). Indeed the transition temperature is reduced to ~50 °C, which is independent of the amount of gold in the films. It is likely that this reduction is caused by strain as a result of preferential orientation as observed previously, indeed the X-ray diffraction pattern has only one significant observable peak, the 011, suggesting a high degree of preferred orientation. It was not possible to perform a meaningful Reitveld analysis as we are only able to observe two

peaks, two smaller peaks in the VO¬2(m) diffraction pattern are obscured by the peaks due to gold. Similarly films that were prepared by sol gel gave transition temperatures of ~55 °C similar to un-doped films prepared by the same method, indeed the X-ray diffraction patterns of these films have a very strong 011 reflection (Binions et al. 2007). By comparison samples of gold doped nano-composites produced by laser ablation and thin films prepared by reactive ion beam sputtering have transition temperatures similar to un-doped vanadium dioxide of around 68 °C, unfortunately no X-ray diffraction data is presented for comparison. As seen with un-doped and tungsten doped samples prepared by CVD a large change in transmission is observable at 2500 nm, typically 35-40% comparable with previous literature values (Binions et al. 2007). The reflectance spectrum is different there is only a small change of around 10% on undergoing the transition. This is attributable to the higher reflectance of the films below the transition temperature, due to the metallic nature of the gold nanoparticles. Un-doped or tungsten doped films of monoclinic vanadium dioxide do not have as significant a metallic contribution to the reflectance and the change at 2500 nm on undergoing the MST is around 35% (Binions et al. 2007).



Fig. 16. (Left) X-ray diffraction pattern of typical Au/VO₂ nanocomposite grown using the hybrid methodology. (Right) Typical SPR hysteresis behaviour of gold-doped vanadium dioxide samples deposited using the hybrid methodology (Binions et al. 2008).

Figure 16 details the temperature dependent hysteresis of the surface plasmon resonance (SPR) band. The SPR band changes with temperature as the rutile and monoclinic forms of vanadium dioxide provide different dielectric environments. The SPR hysteresis behaviour is similar to the optical hysteresis – the hysteresis width is around 20 °C and it indicates a transition temperature of ~ 50 °C. In comparison to SPR hysteresis observed from gold doped vanadium dioxide nano-composites produced by laser ablation (Maaza et al. 2005) the hysteresis width is similar and there is a comparable change of SPR wavelength of 40 nm. The colour of the films (Figure 17) could be altered substantially with a range of blues and greens being produced in contrast to the yellow / brown colour normally associated with monoclinic vanadium dioxide; this is attributed to the inclusion of gold nanoparticles in the VO₂ matrix. The films became bluer in colour with the incorporation of more gold nanoparticles in the films.



Fig. 17. Examples of glass (3 x 5 cm approximate size) with gold and vanadium dioxide nanocomposite films. The films had a V/Au ratio determined by EDAX of: A) 0 (W doped VO₂) B) 0.09 C) 0.15 D) 0.30 E) 0.36 F) ∞ (gold nanoparticle film) (Saeli et al. 2010).

The experimental routes and characterisation of the thermochromic thin films used in this study have been reported previously (Saeli et al. 2010). We have used four different types of thermochromic film in our modelling: pure vanadium dioxide, vanadium dioxide with gold nanoparticles, pure vanadium dioxide grown with a growth directing surfactant, and vanadium dioxide grown with both a growth directing surfactant and gold nanoparticles. These are compared with three standard commercial products, as summarised in table.

The thermochromic coatings were deposited onto Optifloat clear (plain float glass) 4 mm thick glass. Spectral data was recorded using a Perkin Elmer Lambda 950 spectrophotometer. Emissivity data was obtained using a Perkin Elmer PE883 dual-beam IR spectrophotometer, using a NPL calibrated IR mirror as the reference standard. Emissivity was calculated according to standard EN763.

Energy Plus software developed by the Lawrence Berkeley National Laboratory and US Department of Energy was used to perform energy simulations and analysis. Energy Plus[™] is an energy analysis and thermal load simulation program. Based on a user's description of a building from the perspective of the building's physical make-up, associated mechanical systems etc.

A series of simulations with different configurations and settings were run in order to evaluate the performance of the thermochromic coatings in different climates. The simulation set period is one year, with data points gathered every hour.

A very simple model of a room in a building was constructed in Energy PlusTM. The room has external dimensions $6 \times 5 \times 3 \text{ m}$ (length x width x height) and it is placed so that the axis

of every wall is perpendicular to one of the orientation North, South, West and East. We consider the room to represent the façade of a generic building so that just one wall is exposed to the external environment (weather, sun, wind, etc.); the remaining three walls are not affected by external conditions. The building is located in the northern hemisphere and the external wall is supposed to be exposed to the southern side.

Two different glazing possibilities were considered; one where the window was $1.5 \times 2.5 \text{ m}$ located in the middle of the southern wall surface (covering 25% of this surface) considered to represent a residential scenario. The other comprised the whole of the southern face (100%) – a glazing wall, representing a modern commercial building.

Further details governing the materials used for walls etc, have been previously reported (Saeli et al. 2010). In both cases the window is double glazed with a 12 mm air cavity, the coating was always modelled on the inside face of the outer pane. The only difference between each simulation was the glazing or coating used, the 7 examples investigated are summarised in table 2.

Sample	T _c ∕ ⁰C	Cold Visible Transmittance/%	Hot Visible Transmittance/%	Room Temperature Emissivity	Hot State Emissivity
Optifloat Clear (plain float glass)	-	92	92	0.837	0.837
Sputtered Silver Coated Glass (thin metallic coating - SB)	-	82	82	0.030	0.030
Blue Body Tinted Glass (body tinted absorbing glass - AB)	-	76	76	0.837	0.837
Thermochromic 1 (VO ₂)	59	78	74	0.825	0.795
Thermochromic 2 $(VO_2 + Gold)$	43	56	48	0.800	0.752
Thermochromic 3 (VO ₂ + TOAB)	38.5	61	51	0.827	0.789
Thermochromic 4 $(VO_2 + Gold + TOAB)$	45.5	77	49	0.828	0.797

Table 2. Summary of coatings, glass and optical data examined in this study

The external ground temperatures were taken to be 18 °C throughout the year, as this remains relatively constant after a small depth. The internal conditions were chosen to be air-conditioned between 19 – 26 °C to maintain a comfortable working/living environment. The required illuminance level in an office building is taken to be 500 lux, this corresponds to a lighting load of 400 W. The lights are fully dimmable: lowering their output when there is an adequate illuminance from the sun, in order to save energy. It is considered that they can be dimmed in the whole range from 0 to 100 %. The dimming control is automatic and zoned. The casual heat gain (persons + equipment) is taken to be 500 W in total and the ventilation rate used is 0.025 m3/s. Building occupancy was set as occupied from 8:00 till

18:00, five days a week, as is normal for an office. The simulations were run for a number of different cities in Europe and one in northern Africa in order that a wide range of climatic conditions were covered. The specific cities chosen for the simulations were: Cairo (Egypt), Palermo, Rome and Milan (Italy), Paris (France), London (UK), Helsinki (Finland) and Moscow (Russia).

The model is clearly limited because the building is not ideal for all climates. Insulation layers, as well as the materials chosen here, in warmer and cooler climates would be different from that used in the model depending not only on local climate conditions but also on the constructive techniques and materials available in loco. Likewise the assumption that a constant ground temperature of 18 °C throughout the year is significant. However, by using the results obtained from the plain glass (Optifloat) simulations as a baseline we aim to isolate the change in energy performance caused by the use of different glazings.

The thermochromic properties of the glazing were modelled in version 3.0.0 of Energy Plus by entering the spectral data of the glazing in the hot and cold states. The glazing was switched between the hot and cold states using the shading control feature of EnergyPlus which can "replace" glazing elements in a window, according to environment conditions or set control criteria. The surface temperature of the glazing was correlated against incident solar radiation. The shading control automatically switched the glazing from the cold to hot state when the incident solar radiation exceeded that required for the glazing surface to exceed the transition temperature, switching back to the cold state when solar radiation fell below the trigger value.



Fig. 18. (a) Total annual energy consumption and (b) percentage improvement to clear-clear glazing for the 100 % window to wall ratio model;

Cairo, Palermo, Rome, Milan, Paris, London, Moscow, Helsinki.

The total energy consumption improvement for our building is taken as the sum of heating, cooling and artificial lighting energy required for the whole year period compared with a plain double glazed system, these results are presented in figure 18.

The total energy improvement is lower in the coldest cities. This can be explained by the low average temperatures, not allowing the thermochromic glazing to switch for significant periods of time into the hot state. As the thermochromic coatings display insignificant low-e

behaviour (table 2), we would not expect this sort of glazing to be suitable for colder climates. This is illustrated clearly in figure B where the overall performance in cooler climates is not as good as plain float glass.

In warmer climates however the thermochromic glazings perform more favourably than both plain glass and the commercial glazings evaluated here. The best behaviour is shown for thermochromic 3 in the city of Palermo for the 25% window model and in the city of Rome for the 100% window model.

The best overall performance is shown in the 100% window model in cities with warm climates. The thermochromic coatings are a more favourable choice for large glazed areas in these cities. Large glazed surfaces, such as the 100% window analyzed in this work, contribute to a greater percentage to the overall energy balance of the building, potentially minimizing heat losses and as in this case, controlling the incoming solar radiation.

It is interesting to note that the thermochromic 1 glazing, even though it never switches in its hot state because of its high switching temperature, still performs well in the warmer environmental conditions, albeit not as well as the other thermochromic coatings. This suggests that the variable heat mirror properties of thermochromic coatings are not the only important features of these coatings for solar control.

3.3 Use of preformed nanoparticles in hybrid CVD

Nanocomposite thin films of vanadium dioxide and either cerium dioxide or titanium dioxide nanoparticles were deposited using the hybrid AA/APCVD method from vanadyl acetylacetonate and an aerosol of nanoparticles at temperatures between 500 and 600 °C. The deposited films were brown in colour and showed significant surface coverage comparable to that seen previously using this method with vanadyl acetylacetonate [ref]. Compositional analysis of the films performed by EDAX indicated that the films contained vanadium, oxygen in an approximately 1:2 ratio and small amounts of cerium or titanium depending on the nanoparticle solution used. EDAX did not detect any contaminants at least to the limit of detection of this methodology (~1/2 atm%). Experimental conditions and compositional analysis are summarised in table 1. Analysis of film thickness indicated that the films were 850 \pm 50 nm thick, suggesting a nominal growth rate of 42.5 \pm 2.5 nm.min-1. (Binions et al 2007)



Fig. 19. Scanning electron microscope images of nanocomposite thin films samples produced using hybrid CVD.

Scanning electron microscopy of the samples (Figure 19) indicated that the films were formed of large agglomerates. The films made with titanium dioxide nanoparticles (Figure

19B) had agglomerates of 1 to 2 µm in diameter, which are composed of smaller globules of material up to 300 nm in diameter. The films grown with cerium dioxide nanoparticles (Figure 19C) are similar being composed of agglomerates 800 nm to 1 µm in diameter, again these are formed of smaller globules of material up to 300 nm in diameter. In both cases, backscattered electron imaging failed to distinguish the nanoparticles from the vanadium dioxide matrix. In the case of the films grown with the titanium dioxide nanoparticles, this is unsurprising as titanium and vanadium have similar atomic weights and we would not expect to see significant contrast between them. However, in the case of the films grown with cerium dioxide nanoparticles we also cannot detect significant contrast suggesting that the cerium dioxide nanoparticles are highly dispersed through out the vanadium dioxide matrix.

All of the films show thermochromic behaviour with reduced transition temperatures compared to undoped VO₂ single crystals (typically 66 - 68 °C) but are similar to un-doped VO₂ thin films (50 - 66 °C depending on the growth conditions) (Binions et al. 2007). Typically, the hysteresis width of nanocomposite vanadium dioxide thin films is in the range of 15 - 20 °C. Only a small change in transmission is observable at 2500 nm (Figure 20), this is attributed to the thickness of the films. However the reflectance spectrum of the sample (Figure 20) shows a large change of 30 % on undergoing the transition, much larger than is usually observed and is again attributable to the film thickness (Binions et al. 2007).

Methylene blue photodecolourisation experiments were used to gain information on the relative photocatalytic activities of the films. Figure 20 shows the results of these experiments. In all cases, the samples showed better photocatalytic activity than plain untreated glass. The control samples of pure glass and vanadium oxide (sample 1) showed little or no decolourisation of the methylene blue. The pure anatase thin film showed a slow decay over the first 90 minutes (rate = 7.8 x1013 molecules.min-¹), which plateaued thereafter. The inclusion of either titanium dioxide or cerium dioxide nanoparticles into a vanadium dioxide matrix led to a significant increase in photocatalytic activity relative to a sample of pure vanadium dioxide, this does not appear to correlate strongly with the percentage of nanoparticles incorporated into the film. Photocatalytic activity was comparable to that of a film of anatase titanium dioxide prepared by AACVD (Warwick et al. 2010). This suggests that the reactions are limited by the low surface area of the coatings, however, a clear difference between active and inactive coatings can be observed based on initial decolourisation profiles.

Unexpectedly the incorporation of a larger percentage of photocatalytically active nanoparticles did not improve the photocatalytic activity of the films (Figure 20). We attribute this to the fact that film microstructure does not appreciably change with the incorporation of different amounts of nanoparticles in the aerosol portion of the hybrid flow (Figure 20). As nanoparticles are incorporated the films become composed of larger islands, as more nanoparticles are incorporated there is little affect on the film microstructure. Therefore the surface area of the films are likely to remain constant; so even though we would expect a higher number of nanoparticles incorporated to lead to a higher photocatalytic activity this is not the case. A larger proportion of nanoparticles must reside in the bulk of the film rather than at the surface of the film and are unable to influence the photocatalytic activity of the film.



Fig. 20. (a) Methylene blue photocatalysis results and (b) variable temperature optical spectra for nancomposite thin films samples prepared with preformed nanoparticles using the hybrid methodology.

4. Conclusions and outlook

In this chapter we have demonstrated that several new and important CVD techniques are available for the production of nanocomposite thin film materials. We have shown that these methodologies can been used in one step experiments and incorporate preformed nanoparticle solutions or dispersions. The focus of our work has been on architecturally important materials and we have shown that it is possible to synthesise multifunctional films with enhanced properties; although in principle, any combination of matrix material and nanoparticles could be used to produce a wide array of exotic multifunctional nanocomposite thin films. Perhaps more importantly these methods are generally
applicable; CVD is already widely used in the glazing and microelectronics industries this approach could be easily integrated into the production of useful products and devices.

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Polymer Nanocomposites -Fuel Cell Applications

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1. Introduction

"In today's world, solving environmental problems is an investment and not an expense". It is our task in our time and in our generation to hand down undiminished to those who come after us, as was handed down to us by those who went before, the natural wealth and beauty which is ours. Throughout the world, environmental protection *via* green power technology is imperative. It has prompted intensive research activities in various aspects of fuel cells (Sopian & Daud, 2006). Fuel cell is an electrochemical device which directly converts chemical energy into an electrical energy by utilizing various fuels such as hydrogen, methanol, ethanol, methylene blue, glucose, natural gas, etc., in a reaction with an oxidant (oxygen) (Haynes, 2001).

Many investigations have been explored on the various components of polymer electrolyte membrane (PEMFC) and direct methaol fuel cells (DMFC) such as gas diffusion layer (GDL), membrane electrode assembly (MEA), bipolar plates, stack, catalysts, and electrolyte membranes (Bazylak, 2006; Ahmed & Sung, 2008). Among the various components of fuel cells, the research and developmental activities are focusing their keen interest towards the development of polymer electrolyte membranes. Electrolyte membranes act as a separator between the electrodes and determine the over all performance of fuel cells. In other words, electrolyte membranes are considered as the basic backbone or heart of the polymer membrane electrolyte fuel cells. High tempearture and lower humdity operation of fuel cell is essential for the higher energy perfomance and it circumvents the reformer which decreases the cost of the entire fuel cell device. In general, acidified polymers have been used as a polymer electrolyte membrane for the applications of fuel cells. The higher extent of acidification leads to a physical infertility and deteroites the fuel cell performance and durability. So an improvement has to be made on the polymer membrane for the betterment of extended fuel cell performance associated with the durability. Though many efforts have been addressed to gear this issue, synthesis of new proton conducting polymers and modifying the existing polymers with nanometric inorganic filler techniques are very attractive. The difficult molecular and structural parameters of the new polymer synthesis hinder its large scale applications. Whereas easier and controllable synthesis routes

associated with cheap cost and less environmental impact of polymer nanocomposite influences its viable applications in fuel cells.

The polymer nanocomposites are polymer matrices reinforced with nanometric inorganic fillers and are an integral aspect of nanocomposite technology. Polymer nanocomposite materials are remarkable family of isotropic, flexible, amorphous nanocomposite materials, which have been extensively investigated for structural materials and biomedical materials due to their enhanced optical, electrical, thermal, magnetic, physical, chemical, conductive and other smart functionalities (Ahmed & Sung, 2008). Recently, numerous polymer nanocomposite membranes fascinate the fuel cell field (Karen & Richard, 2007). The prerequisites of polymer electrolyte membranes can be effectively satisfied by synergistically combining both organic and inorganic nano materials. The prepared composite materials possess enhanced properties compared with the single organic or inorganic material. Main concept of the development of nanocomposite membranes is to acquire the best properties of the components and trying to eliminate the drawbacks of an individual component by the synergetic interaction. A specific interaction involves between the organic and inorganic components influences the electrochemical stability. The hygrospoic characteristics of the included nanomaterials adsorb water molecules in a greater extent, stores in its voids and has become responsible for the lower humidity operation. The proton transfer takes place on the surface of the inorganic particles and a high surface area of fillers increases surface area of the membrane which in turn improves the surface chemistry. Whereas ceramic property of the nanofillers influence higher temperature applications. Thus the polymer nanocomposite material influences high temperature and lower humidity operation of fuel cells with an extended durability.

Polymer nanocomposite's properties and applications in fuel cell is a valuable reference tool for both the research community and industry professionals. This chapter is aimed to project the efforts carried out, preparation, mechanism and future proposectives of polymer nanocomposites applicable for fuel cells.

2. Requirements of polymer electrolyte membranes

The favorable properties of polymer electrolyte membranes for the efficient fuel cell performances are described as follows:

2.1 Ionic conductivity

Ionic conductivity is defined as the capability of the transportation of ions which determines the power generation of a fuel cell. Catalyst (Pt for PEMFC and Pt-Ru for DMFC) loaded on the electrode splits the fuel (H₂/methanol) into ions and electrons and the membranes have to conduct ions through its viable channels which are created for the effective passage. Ionic migration includes transportation of protons and other species such as OH-, H₂O, H₃O⁺, NH₄ ⁺, HS⁻ etc., Ionic conductivity effectively determines the over all efficiency of fuel cells. Ionic conductivity of the membranes highly depends on the operating temperature and relative humidity conditions. Increase in the temperature promotes the flexibility of the membrane by the structural reorganization which favors the faster ions migration. If the operating temperature exceeds the membranes dew point, a dramatic drop in the conductivity is observed for the perfluoro sulfonated membranes due to the evaporation of water molecules. Relative humidity also plays a vital role in the determination of ionic conductivity. Increase in the relative humidity humidifies the polymer chains and lowers the viscosity of the membrane and leads to a higher water content in the electrolyte which presumably raises the ion mobility and conductivity (Li et al. (2003).

2.2 Fuel permeation

Fuel crossover is the major draw back of fuel cells which decreases the fuel cell efficiency by poisoning the cathode catalyst and slows down the electrode chemical reaction. Fuel oxidation kinetics has become sluggish due to the high fuel crossover. It renegades fuel crossing from the anode to the cathode catalytic layer and hampers oxygen reduction at the cathode. The approaches which were made up so far to reduce the fuel cross over were not effective in both PEMFC and DMFC. Though the lowering of temperature and the dilution of fuel (in DMFC) results in diminution of fuel crossover, it considerably decreases the efficiency of fuel cells *via* the minimal ions transportation. Increase in temperature and back pressure enhances the fuel permeation and when it comes with respect to relative humidity fuel crossover has become much more complicated. At lower temperatures increase in relative humidity results in the increment of fuel crossover due to its high level of water content. But sometimes at higher temperatures increase in relative humidity results in a decrement of fuel crossover. Further researches should be applied to analyze this parameter. Low level consumption of fuel is an important factor for the high performance of fuel cells. So fuel crossover should be lowered for the lesser fuel consumption which effectively enhances the performance of fuel cells (Neburchilov et al. 2007).

2.3 Mechanical stability

When the membrane contacts with the fuels especially liquid fuels, swelling ratio of the membrane gets enhanced which diminishes the mechanical stability. For the fabrication of membrane electrode assembly (MEA) and fuel cell applications, the membrane has to be highly strengthened. Hydrophobic property of the membranes supports the mechanical integrity but also hinders the ion transport. The function of hydrophobic phase is to prevent water from "pooling" within the pore volume of the backing layer so that gases can freely contact with the catalyst sites. Furthermore, it facilitates the removal of water molecules on the cathode as it creates a non-wetting surface within the passages of the backing material to avoid mechanical infertility. For the immurement of ionic conductivity and other electrochemical properties, hydrophilic phases are included in the membrane which consequently decreases the mechanical stability. So fuel cell membranes should be designed to contain major hydrophobic part for the betterment of mechanical integrity.

2.4 Thermal stability

Operating conditions of a fuel cell widely depend on the thermal management. Thermal management improves the kinetics of oxidation reaction and tolerates the exhausted carbon monoxide. It controls the cooling system and maintains a good hygrometry level within the fuel cell system. High operational temperature of fuel cells is proximally equal to the methanol reforming and hydrogen desorption which greatly circumvents the need of additional systems such as methanol reformer and hydrogen storage capacitors. The integrated system leads to a higher efficiency, smaller size, high reliability, and simple construction. Though PEMFC and DMFC are being operated at lower temperatures, polymer electrolyte membrane's thermal stability should be opt to be applied in fuel cells. Operational temperature difference to cool the air efficiently. Glass transition

temperature of the membranes should be higher than that of operation temperature of fuel cells for the betterment of electrochemical properties.

2.5 Durability (lifetime)

The main advantage of fuel cells over the conventional batteries is as long as fuel supplied to the cell it generates electricity. But the lifetime of commercially available membranes is not adequate for the fuel cell commercialization. Even the operation temperature exceeds 100°C, lifetime of the membranes should be enhanced to a couple of months. Compatibility between the electrode layers and membrane effectively determines the durability of the fuel cells (Cho et al. 2005).

2.6 Fabrication cost

For the commercialization of fuel cells, cost of the electrolyte membranes has to be controlled. So far, cost of the commercially available membranes is consuming almost the cost of an entire fuel cells device (Tricoli & Nannetti, 2003). Nafion membrane remains quite expensive with production costs of about US\$800/m². Though the membranes are commercially available in the market, to bring forth fuel cells in a global level more significant efforts should be devoted in this area. A short version of the aforementioned favorable properties for the efficient fuel cell performance is depicted in Table. 1.

Proportios	Increase in operating conditions					
	Thickness	ess Temperature Relative humidity		Fuel concentration		
Water content	Ļ	Ļ	↑	↑		
IEC	Ļ	1	↑			
Mechanical stability	↑	Ļ	↓ ↓	↓		
Conductivity	Ļ	1	↑	↑		
Fuel permeability	Ļ	1	↑	↑		
Cell performance	Ļ	1	↑	1		
Life time	↑	Ļ	↑	Ļ		
Emission of gases		Ļ		1		

Table 1. Favorable properties of the polymer electrolyte membranes for the efficient fuel cell performances.

3. Criteria for the selection of inorganic nanomaterial

i. Hygroscopic characteristics

Hygroscopic characteristic is one of the most influential property for the polymer nanocomposite which effectively determines ion transportation of the membrane. Though the acidified polymer influences water adsorption characteristic, structural, bonded and adsorbed water molecules of nanometric fillers alone can effectively influence the aforementioned property. Since the water molecules present in the membrane determines the ion mobility, fillers have to be chosen based on their strong hygroscopic properties.

ii. Ceramic property

As aforementioned, the fuel cells have to be operated at higher temperatures. A higher acidification degree of a polymer obliterated the thermal stability which inturn lowers the fuel cell operation temeparture. Nanoparticle's ceramic effort influences the thermal stability of a polymeric backbone which inturn promotes the operational tempearture. So a higher ceramic effort of nanoparticle may influence its viable applications.

iii. Porosity and pore connectivity

The water molecules adsorbed by the inorganic fillers have to be stored in the surface of the nanofillers. Since porosity is directly proportional to the water adsorption, extended porosity is essential for the higher water adsorption. In addition, a strong interconnection between the pores facile the continuous ion transportation.

iv. Surface area

The electrochemical performance of a system is purely dependent upon the surface area of the constituted materials. Though the host polymeric material may have surface area, a further increment in the surface area of the material *via* nanofillers may influence the system's electrochemical performance. So the inorganic fillers should be prepared to possess higher surface area.

v. Additional ions

The additional ions given *via* surface of the nanomaterial promote the number of ion migration which inturn influences ionic conductivity of the membrane. This criteria is effectively done by the acidified hygroscopic fillers and protonic conductors.

4. Preparation of polymer nanocomposite techniques

The polymer nanocomposite membranes which are applicable for fuel cells have been prepared by the following techniques.

i. Casting of polymeric nanocomposite solution

Solution casting is one of the simplest methods for the preparation of nanocomposite membranes. A few microlitres of a dilute solution containing the dissolved polymer and nanofillers are cast as a film followed by the evaporation of a solvent. It enables direct incorporation of nanosized inorganic materials into a polymer matrix and a number of nanocomposite membranes have been prepared using this procedure. In a typical experimental procedure, appropriate amount of nanoparticles are first mixed with the polymer solution under vigorous stirring. The membrane is then obtained by film casting and dried until all the solvent get evaporates (Gnana kumar et al. 2007). For bulk mixing, the inorganic components should be prepared in the form of powders or dispersions. It is an easier process and the thickness of the membrane could be easily controlled. But a physical interaction exists between the polymer and nanomaterial has left few questions such as inhomogeneities of the composite membrane and the formation of pores around the oxide particles and may leach out under the repetitive cycles.

ii. Sol-Gel

Sol-gel process is a versatile technique for the preparation of proton-conducting nanocomposite materials. Direct mixing of precursor solution with the organic polymer leads to the formation of proton conducting membranes. A hybrid structure is obtained at the molecular level with entirely different properties by co-polymerization of inorganic monomer in the presence of organic polymeric solution under the proper solvent and catalyst. The general methodology used to prepare these membranes is coined as a sol-gel process (Nagarale et al. 2005).

e.g: Mixing of organic polymer solution with organometallic precursors such as Tetramethoxysilane (TMOS), Tetraethyl orthosilicate (TEOS), Zr(IV)-propoxide, Ti(IV)-butoxide, etc. by hydrolysis and condensation in presence of suitable catalysts, acid or base.

iii. Insitu impregnation process

Insitu impregnation process is a versatile technique for the preparation of low cost protonconducting nanocomposite materials. A homogeneous natured membranes obtained at lower temperature from this technique influences its potential application. The membranes are impregnated in the inorganic material's precursor solution and the process begins with its incorporation. The nucleophilic attack of the water present in the membrane on the inorganic atoms leads to the hydrolysis of the infiltrated inorganic precursor and membranes have to be treated with necessary reactants for the condensation process. If the reaction is an acidcatalyzed hydrolysis, and the acidified polymer which possesses the pendant SO₃-H⁺ group will itself act as a catalyst, and the need for external reactants has been circumvented. The impregnation of polymer membranes with inorganic precursors experienced a difficulty in maintaining concentration gradient of precursor solutions which virtually limits the incorporation of inorganic components into the polymer matrix to a certain level.

e.g : Nafion membrane modified with tetra ethyl orthosilicate (TEOS) (Kelarakis et al. 2010).

iv. Covalent Binding

Synthesis of polymer nanocomposites *via* the formation of covalent bonds between aromatic polymers and inorganic clusters is an effective approach in the development of proton-conducting membranes for fuel cell applications. This approach requires molecular precursors that contain a hydrolytically stable chemical bond between the element that will form the inorganic network during sol–gel processing and the organic moieties.

Organic components can be chemically modified to covalently attach the inorganic network, e. g. silylation. The organic components after silylation are easily accessible to common hydrolysis and polycondensation reactions. The primary aim is to synthesize a polymer containing both -SO₃H functions and silicon moieties. The order of the synthesis steps is (i) Sulfonation , (ii) Silylation and (iii) Sol-gel process

A novel, efficient and experimentally simple method for the introduction of silicon functional groups into polymeric carbon frameworks is to combine the features of a cross-linked polymer and the presence of covalent organic-inorganic, C-Si, bonds in one macromolecule (Vona et al. 2006). Cross-linking can be obtained during the sulfonation step by formation of SO_2 bridges among the repeating unit of PEEK.

The synthesis route follows the given steps :

Step 1. Direct sulfonation of PEEK with chlorosulfonic acid (ClSO₃H); this will result in SOPEEK

- sulfochlorinated PEEK

Step 2. Silylation – this will introduce covalently linked silicon moieties in SOPEEK

Step 3. Hydrolysis of sulfochlorinated PEEK in order to obtain the desired -SO₃H functions SOSiPEEK)

v. Polymerization process

For the ideal ionic membrane, hierarchically ordered ionic channels/particles should orient vertical to the membrane surface. This can be achieved only *via* surface-initiated atom transfer radical polymerization (ATRP). Ordered two-dimensional macroporous silicon renders proton conducting membrane by growing a thick uniform polyelectrolyte brush using surface initiated atom transfer radical polymerization throughout the porous matrix (Yameen et al. 2009).

<u>e.g</u>: Firstly, a macroporous silicon scaffold is modified with the self-assembled monolayers of 2-bromo-2-methyl-N-(3-triethoxysilylpropyl)propionamide. Then the macroporous membranes with polymer brushes were copolymerized by sulfopropyl methacrylate (SPM) and monomethoxy oligo- (ethylene glycol) methacrylate (MeOEGMA) and the membrane channels were completely filled with polySPM-co-MeOEGMA brushes, thus indicating that the surface-initiated copolymerization proceeded smoothly in the confined environment of the membrane channels. It has been demonstrated that the synthesis of hybrid membranes by pore-filling surface polymerization is a new approach to create proton-conducting channels with tailor-made and finely tuned physicochemical characteristics.

5. How does the polymernanocomposite satisfy the requirements of electrolyte membrane applicable for fuel cell?

Polymer nanocomposite has already been proved as an effective technique for the empowerment of higher temperature and lower humidity fuel cell applications. The significant improvements which have been made on the polymeric membranes to support /empower the higher temperature and lower humidity fuel cell applications are given as follows:

5.1 Water adsorption and retention

The nanometric inorganic fillers present in a composite bind larger amount of water molecules with the membrane *via* its hygroscopic effort. The voids or cavities which are present in the inorganic fillers influence higher amount of water adsorption and tightly pack the water molecules in its voids. The higher amount of water molecules present in the membrane humidifies the polymeric units or channels which in turn favors the lower humidity operation and also circumvents the usage of a humidifier. Though the operational temperature of fuel cells exceeds 100°C, a tight packing of water molecules achieved *via* nanofiller influences water retention of the composite membrane. Thus it declines the major drawback of Nafion membrane's protonic conductivity decrement at high temperatures and facilitate the higher temperature fuel cell applications.

5.2 Ionic conductivity

The most trifling case in ionic conductivty mechanism is the assistance of proton migration by the translational dynamics of bigger species. The proton diffuses together with a vehicle (e.g., as H_3O^+) where the counter diffusion of unprotonated vehicles (e.g., H_2O) allows the net transportation of protons. The relevant mechanism is called as vehicle mechanism. Increase in the temperature diminishes the hydrogen bonding between water molecules which distinctly reduces the proton jump in Grothus mechanism. In many cases, Grothus type mechanism is progressively dominated by vehicle-type mechanisms at increasing temperature, i.e. there is a gradual transition from Grothus to vehicle type conductivity (Lorrain et al. 1996). The higher amount of water molecules adsorbed by the nanofillers promote the aforementioned mechanisms. A higher amount of absorbed water molecules solvate the acid moieties of a polymer in a greater extent and facilitate the hydrogen bonding among/between water molecules and has become responsible for the higher ionic conductivity. In addition, protonic conductor added swollen membrane induces additional protons *via* its surface which promotes ionic conductivity of the membrane further.

5.3 Fuel cross over

As aforementioned, fuel permeation is a major drawback of fuel cells. A high protonic conductivity-methanol permeability selectivity ratio is an effective parameter for the efficient fuel cell performances. But higher fuel permeation decreases the selectivity ratio and there by fuel cell efficiency by poisoning the cathode catalyst and slows down the electrode chemical reaction. The addition of fillers effectively blocks the molecular passage (Fig. 1). For the filler free membrane, methanol molecule can be easily transported without any hindrances. But the fillers (ceramic and protonic conductors) create tortous path ways for the molecular transportation, reduces the electro osmotic drag which effectively dries the membrane at the anode side and suppresses the flooding. It has been observed that the cross over current measured with the modified membrane in an order of magnitude lower than that of the unmodified polymer membranes (Ahmad et al. 2010; Gnana kumar et al. 2007).

5.4 Thermo and mechanical properties

Though ionic conductivity and fuel permeation play a decisive role in the determination of fuel cell efficiency, thermal and mechanical stabilities have also to be considered. Though higher acidification degree of a polymer is responsible for the higher ionic conductivity, it deteriorates the thermal and physical stabilities. So a compromise has always to be taken between the mechanical and electrochemical properties. In order to increase the thermal and mechanical stabilities, acidification degree has to be lowered. But it leads to a lower ionic conductivity and lower electrochemical performances. By keeping the high ionic conductivity of a polymeric membrane, physical and mechanical stabilities have to be strengthened. Thermal stability of the polymeric membrane is influenced by the nanofiller *via* its ceramic effort (Neburchilov et al. 2007). It is also evidenced that the Tg and Young's modulus of the polymer are improved by the incorporation of inorganic additives.

5.5 Fuel cell performance

Due to the increased water retention, high ionic conductivity associated with the lower fuel permeability of the polymer nanocomposite electrolyte membrane results in better electrode performance at high temperatures and lower humidities. Thus it has been reported that nanocomposite membrane exhibited 5-10 magnitude greater performance than that of bare polymer membrane.



Fig. 1. Proposed ion transportation and fuel cross over mechanisms of (a) bare polymer, (b) polymer-ceramic filler nanocomposite and (c) polymer-nanoprotonic conductor composite membranes [(—) methanol, (•••••) ions and (••••••) additional ions]

5.6 Durability

Incorporation of hygroscopic oxides improves lifetime of the membrane by enhancing the corresponding membrane's physical stability. Hygroscopic oxides fix the acid functional group within the membrane and do not allow the electrolyte to leach out and thus ensure the durability of the polymer membranes (Neburchilov et al. 2007). The nanocomposite membrane extended the durability of bare polymeric membranes for a couple of months.

5.7 Easier fabrication techniques

Complex synthesis methods are the major hindrances for the preparation of new polymers. It has directed the researchers to work on the modification of existing polymers. Among the various techniques proposed, polymer nanocomposite has well known for its easier and controllable fabrication methods.

6. Polymer nanocomposite membranes

6.1 Perfluorinated nanocomposite membranes

The concept perfluorinated polymer nanocomposite for fuel cell applications was developed by Watanabe et.al (Watanabe et al. 1994). Though Nafion membrane is considered as a standard bench mark of all kind of fuel cell membranes due to its elevated chemical, thermal and physical stabilities, it exhibits few limitations such as high temperature and lower humidity operation difficulties. Various efforts have been explored on the development of new polymer electrolyte membranes. But none of them can compete with the Nafion membrane at a large scale level. Instead of developing a new kind of polymeric membranes, the modification of commercially available membranes can create wonders. Perfluorinated polymer nanocomposite membranes can be prepared either by (1) casting a bulk mixture of powder or colloidal inorganic components with a polymer solution, or (2) *in-situ* formation of inorganic components in a polymer membrane or in a polymer solution. Inorganic components are prepared in the form of powders or dispersions for bulk mixing. Transfer of this colloidal suspension into a polymer solution should enable inorganic particles of nanometer size to be dispersed in a formulated membrane. Sometimes colloidal suspensions can also be utilized for bulk mixing. Other techniques such as exchange-precipitation and sol-gel reactions are also effective for the preparation of composite membranes.

i. with hygroscopic oxides

As discussed, high ionic conductivity of Nafion membranes has been facilitated by the high retention of water molecules in the membrane. The water molecules retention is facilitated by the hygroscopic oxides such as silica (SiO₂), titania (TiO₂), alumina (Al₂O₃), and zirconia (ZrO₂). Water adsorbed on the surface of the oxides effectively decreases the electro-osmotic drag by enhancing the back diffusion of the cathode produced water. Hygroscopic oxides can act as self-humidifying agents. The humidification of Nafion membrane is effectively done by the hygroscopic oxides and inclines the utilization of a separate humidifier.

Antonucci et al. (1999) improved the power density of Nafion up to 240 W cm-2 at 145°C by the incorporation of silica. Though the fuel cell operation temperature exceeds 100°C, performance decay was not observed for the modified Nafion membrane due to the inclination of membrane dehydration phenomenon (Antonucci et al. 1999). Dimitrova et.al. modified Nafion with a high boiling point solvent (dimethylsulfoxide or 1-methyl-2pyrrolidon) and silica. The incorporation of hydrophilic inorganic particles retained more water content and influences the water transfer to the cathode. The higher water uptake brings about a size growth of the ionic clusters and pores which effectively determined the transport properties of the membrane. The modified membrane structure consists of the broader water filled channels with more separated and less branched channels and pores which correspond to a smaller hydrophilic-hydrophobic interface and smaller average separation of sulfonic groups. It leads to an increased ionic conductivity even under higher temperatures (Dimitrova et al. 2002). Miyake et.al. modified Nafion 117 membrane with silica via sol-gel technique (Miyake et.al. 2001). The enhanced water uptake of the modified hybrid membranes than that of pure Nafion is attributed to the strong hygroscopic effort of silica. The tensile strength of the silica modified membrane was 5.4×10^3 psi which is much higher than unmodified membrane whose tensile strength was 3.2×10³ psi. By the simple hydrolysis and condensation of alkoxysilanes, inorganic phase has grown inside the organic matrix based on the sol-gel process. The condensation and hydrolysis of TEOS promoted the growth of a silicon oxide phase inside the Nafion clusters. TEOS included in Nafion through sol-gel process influences water uptake which favors ionomer structure, cluster and channel size. The modified Nafion membrane exhibited four times higher current density than that of unmodified Nafion at 130°C under 3 atm pressure (Miyake et.al. 2001). Jiang et al. modified the Nafion membrane by silica through sol-gel technique. Though the conductivities achieved for the composite membranes are inferior to the Nafion membrane, lower methanol permeability in the range of 4.17×10^{-7} cm² s⁻¹ achieved for the 5 wt.% silica loaded membrane with the higher thermal stability influence its viable application (Jiang et al. 2006). At lower silica loadings, the hydrophilic silica particles may mainly exist around the hydrophilic ioncluster and the ion channels. Addition of silica particles increases tortuous nature of the methanol transport channels by changing the microstructure of Nafion. The cell voltage of 5 wt.% silica composite membrane was increased due to the lower methanol crossover (Jiang et al. 2006). There after number of efforts and patents (Adjemian et al. 2006)has been filed on the modification of Nafion with hygroscopic oxides. Other hygroscopic oxides such as titania, alumina and zirconia were also extensively utilized for the modification of Nafion. Incorporation of hygroscopic oxides to the Nafion membrane, leads to a self- humidification, reduces the fuel permeation and eventually enhances the fuel cell performance. The size of polar ionic clusters of Nafion membrane is about 3-5 nm. So the hygroscopic filler size which have to be incorporated in to the polar matrix should be lesser than the nation membrane's polar cluster size. The effectively panneled hygroscopic fillers in the Nafion polar clusters alone can influence the electrochemical properties.

ii. with protonic conductors

The purpose of the inclusion of hygroscopic oxides into the Nafion membrane is only/mainly to retain the water molecules. But the incorporation of protonic conductors effectively satisfies both high water retention and provision of additional ion sites in a greater extent. Nafion membranes modified by the proton conductors exhibited excellent properties and are described as follows:

A simple method for the preparation of inorganic proton conductor-PFSA composite membranes is obtained from the casting of an ionomer solution containing proton conductor compounds. This is a well known method and adopted by many researchers in general. On the other hand, exchange precipitation method is under the rapid subject enrollment in the Nafion membrane modification field. For this process, Nafion membrane is first swollen in a boiling methanol-water mixture and then soaked in a zirconyl chloride solution at 80°C. In this way Zr⁴⁺ ions are introduced into the ionic sites of the membranes by ion exchange method. Then according to the desirable functionality, membranes can be activated either with phosphoric acid or sulfuric acid (Grot & Rajendran, 1999). The pores of Nafion membrane trap the proton conductors for the plausible ionic conduction. Proton conductors enhance the water retention characteristics and increase the operational temperature of fuel cells. A strong influence of the protonic filler concentration on mechanical properties as well as the thermal properties was also observed.

The surface area of Nafion membrane was increased two orders of magnitude by the inclusion of zirconium phosphate. C. Yang et.al modified the Nafion 115 membrane *via* an exchange reaction involving Zr^{4+} ions followed by precipitation of zirconium phosphate. Under the low humidification conditions, the maximum power densities achieved at 145°C with these MEAs were 375 and 260 mW cm⁻² in the presence of oxygen and air, respectively. The best fuel cell performances were observed for the composite membranes under the lower methanol preheating temperature and lower humidification cathode gas feed conditions. It simplifies the auxiliary systems and eliminating the requirement to vaporize the necessary quantities of water for humidification, as required by conventional systems with the improvement of water retention (Yang et al. 2001). Bauer et al. modified Nafion 117

membranes with zirconium phosphate. The ionic interaction between the filler and the hydrophilic clusters was very strong which reduced the ability of the back-bone regions of Nafion to align into crystallites. It leads to a strong influence on both the mechanical properties and glass transition temperature of the corresponding hybrid membranes. When the operation temperature exceeds the glass transition temperature of a Nafion membrane, a significant damage occurs usually in the membrane, and was successfully prevented by the addition of protonic conductors (Bauer et al. 2004). A decrease in the methanol permeation leads to a high ionic conductivity-fuel permeability selectivity ratio which eventually promoted its viable application in DMFC.

iii. with carbon nanotubes

As aforementioned, high cost of the Nafion membrane hinders its commercial application in a large amount. Thinner membranes have been introduced to reduce the cost of electrolyte membrane. Decrease in the thickness not only leads to a reduction in the cost but also escorts to a reduction in the resistance of a membrane. However a decrement in the thickness facilitates a mechanical infertility which eventually lowers the durability. To endure the thinner membrane's stability, Nafion membranes were modified with carbon nano tubes. Carbon nanotubes (CNT) are considered as the ideal reinforcing fibers due to their unique one-dimensional structure and a range of fascinating properties such as exceptional mechanical properties, low density, high aspect ratio, unique nano porous structure, high specific surface area, and tunable properties etc.,. But the main draw back of CNT inclusion in Nafion matrix is the high risk of short-circuit caused by a non electrically isolated electrolyte. But it can be tackled by keeping the lower content of carbon nanotubes than the percolation threshold.

Liu et al. developed Nafion-multi walled carbon nano tube composite for the PEMFC applications. It has been reported that an inclusion of carbon nano tubes with the Nafion ionomer increases the mechanical strength from 22.08 to 37.08 MPa. A good compatibility exhibited between CNT and Nafion matrix results in restraining the swelling of a membrane and improved the mechanical strength. At the mean while, a low content of CNT doesn't affect the ionic conductivity of the membranes. A low CNT content neglects the short circuit and results in a comparable fuel cell performance as that of pure Nafion membrane (Liu et al. 2006). Thomassin et al. reported that an inclusion of MWCNT decreases the methanol permeability due to its better dispersion. An increase in the length of the CNT reduces methanol permeability in a large amount and also accounts for the higher mechanical strength. Though a decrease in the ionic conductivity was observed for the composite membranes, a larger reduction in methanol permeability accounts for the high conductivityfuel permeability selectivity ratio and ensures its appliances (Thomassin et al. 2007). Kannan et al. observed that the acidified single walled carbon nano tubes enhanced ionic conductivity and activation energy of the Nafion membrane. The extra sulfonic acid moieties anchored on the surface of the CNTs could facile the hopping of protons, which in turn would help to increase the proton mobility and accounts for the high ionic conductivity. An increase in the acid-water clusters of the recast Nafion membrane decreases the charge-transfer resistance which in turn enhances a power density of 260 mW cm-2 at 0.42 V which is far ahead of pure recast Nafion membrane. Though high ionic conductivity was facilitated for the composite membrane, physical yield point was also improved (mechanical stability) through the governance of CNT features (Kannan et al. 2008).

6.2 Hydrocarbon membranes

In addition to the modification of commercially available membrane Nafion, various efforts have also been addressed on the several kinds of polymers. Poly ether ether ketone (PEEK) based membranes were developed to contain hetero poly acids and an oxide phase. It was either produced by hydrolysis of amino-modified silanes or by dispersion of surface modified fumed silica. Though hetero poly acid possesses good proton conductivity, it has shown degradation in the DMFC applications due to its dissolution in water. The stability has usually been increased through silica modification which increases the strength of the covalent bonds or columbic interactions but reduces the acid strength. By the addition of silanes and the dispersion of surface-modified silica, leach out of hetero poly acid can be effectively reduced.

Karthikeyan et.al. modified the SPEEK membrane with different forms of silica such as laponite (a synthetic layered silicate), aerosol (spherical nano particle), and MCM-41 (acid silicate with mesoporous structure). The 10% MCM-41 included membrane exhibited better conductivity and reasonable fuel permeability among the studied membranes. This was achieved by the effective formation of pathways between the filler and polymer matrix due to its high compatibility. In general, the polymer chain strongly interacts with silica or silanol through hydrogen bonding. It results in the enhanced mechanical stability of the hybrid membranes (Karthikeyan et al. 2007). Kalappa et al. developed SPEEK/TiO₂ membrane with reduced methanol permeability. The weaker hydrophilicity of the polymer, higher concentration of rigid backscattering sites, and increased tortuous pathways for the molecules to encounter during permeation were created by the TiO₂ inorganic particles. It blocks the molecular passage and resulted in the lower fuel permeability. The included inorganic particles prevent the reactant loss, enhance the power density, and guaranteed the long-term membrane stability (Kalappa et al. 2007).

The most extensively studied protonic conductor in the fuel cell field is zirconium phosphate (ZrP). Two predominate structures of *a*-zirconium hydrogen phosphate and γ -zirconium hydrogen phosphate are available. The hydrogen bonded network of water is achieved due to the pendant OH group and the interlayer region of *a*-ZrP. At the mean while, the γ -ZrP has the advantage of having an extra water molecule per formula unit and is more acidic than the *a*-ZrP. Inclusion of protonic conductors enhances the water content of the membrane and also provides the additional ions. A three fold improvement in conductivity was achieved for the 10 wt.% *a*-ZrP loaded SPEEK membrane. Using the bulk mixing method, composite SPEEK membranes were prepared with zirconium phosphate and sulfophenyl phosphonate. Conductivities of 0.09 S cm⁻¹ at 100°C and 0.04 S cm⁻¹ at 150°C under 100% RH were reported for these membranes (Bonnet et al. 2000).

Silva et al. synthesized hybrid SPEEK membrane with ZrP/PBI. The inorganic incorporation of pretreated zirconium phosphate decreases the membrane proton conductivity, aqueous methanol swelling, and methanol permeability. But the high proton conductivity-methanol permeability selectivity ratio obtained in these membranes resulted a maximum power density and current density of 50.1 mW cm⁻², 250 mA cm⁻², respectively under 130°C (Silva et al., 2005). Hickner et al. developed sulfonated polysulfone phosphotungstic acid hybrid membrane and the ionic conductivity and mechanical modulus of the material was improved by the addition of inorganic particles (Hickner et al. 2001). Dimitrova et al. incorporated phosphate antimonic acid particles into sulfonated polysulfone. The fabricated membranes exhibited the improved mechanical properties and conductivities close to Nafion were obtained with the absence of excessive water swelling at 80°C (Dimitrova et al. 2001). Cesiumphosphate is a promising protonic conductor that has a bulk conduction mechanism. Increase in the temperature beyond 140°C changes the monoclinic structure of cesiumphosphate into a tetragonal structure which leads to an increase in the conductivity by 2–3 orders of magnitude and is often referred to as a "superprotonic" transition (Haile et al. 2001). Recently, Sunarso et.al. blended titanium zirconium phosphate into the polyvinyl alcohol and ethylene glycol matrix. 50 wt.% of titanium zirconium phosphate content enhances the ionic conductivity up to 0.25 S cm⁻¹ which is three orders magnitude greater than the PVA membranes (Sunarso et al. 2008). The functionalized inorganic phase dominated proton conduction which may be attributed to a higher freedom of charge carriers due to the acidic groups of the inorganic phase, instead of just relying on the polymer bonds.

6.3 Acid-base membranes

In general, acid-base membranes involve the incorporation of an acid with the alkaline material. For the immurement of electrochemical properties, most of the polymer electrolyte membranes possess acidic functional groups. The high ionic conductivity of the sulfonic acid group is achieved by their strong attractive forces with hydrogen ions. In order to improve its affinity towards water than methanol, it is being incorporated with the basic polymers such as polyvinylalcohol, polyethyleneoxide, polyacrylamide polybenziimidazole, polyaryleneether, and polyether ketone. The polymers contain functional groups such as alcohol, amide/imide, ether, ketone which are purely meant as the basic sites. The basic functional group reacts with acidic functional group by the establishment of hydrogen bonds. In other words, acid dissociates in the basic polymer which acts as a solvent. The polymer electrolyte membranes which are made up of acidic functional groups possess high ionic conductivity due to their strong attractive forces with hydrogen ions. Because of phosphoric and sulfuric acid's unique proton conduction mechanism by self-ionization and self-dehydration, it exhibits the effective proton conductivity even in their anhydrous form. Though ionic conductivity of the acid-base membranes are ensured by the sulfonic acid attachment, higher ionic conductivity and improved mechanical properties are under crisis for the acid-base membranes.

The sulfonic acid functionalized polymer nanocomposites based on PVA/SiO₂/sulfosuccinic acid (SSA) were reported. In the hybrid membranes, sulfosuccinic acid served as both sulfonating as well as cross-linking agent. The proton conductivity and methanol permeability of the hybrid membranes were studied with changing SSA content from 5 to 25 wt% and found very much depends on SSA content. They found proton conductivities in the range of 10-3 to 10-2 S cm-1, and the methanol permeability 10-8 and 10-7 cm2 s-1 range. They claimed the decrement in methanol permeability in the presence of silica particles. In course of finding, inclusion of SSA decreases the crystallinity of the membrane and an inclusion of silica decrease the crystallinity further. The segmental mobility of polymer chains is much higher in amorphous regions than the crystalline. The amorphous nature produces greater ionic diffusivity in accordance with the high ionic conductivity which can be obtained in amorphous membranes that have a fully flexible backbone (Kim et al. 2004). In general, a decrease in the crystalline nature effectively increases the flexibility of the polymeric backbone and promotes the ion transfer. Gnana kumar et.al studied the particle size effect on the ionic conductivity properties. A decrease in the nanometric size of silica filler enhanced the ionic conductivity of the polymer nanocomposite. The critical nucleation radii of nanoparticles are larger than the particle diameter. But the structural transitions can occur only with the larger particle radius than the critical nucleation radius. These transitions can easily occur with the smaller size

particles and yields to the structural changes (Gnana kumar et al. 2009). With an account of surface tension, the unique properties are so strong in the vicinity of surface (shell region), while they are in bulk it is strong enough in the central part of a particle (core region). Since the ratio of the shell to the core contribution increases with the decrease in the particles size which allowed to increase the ionic conductivity of the prepared composite membranes. Decrease in the filler size enhances the surface area which effectively creates a new route for polymer-filler interface and yielded the high ionic conductivity. Among the hybrid membranes, 90 nm silica filler incorporated hybrid membrane exhibited the high ionic conductivity. This study has directed the polymer nanocomposite researchers to study the influence of size, shape and phase of the nanomaterials on electrochemical and physical properties.

Similarly, composite membranes of PVA/SiO2 with copolymer of 2-acrylamido-2-methylpropanesulfonic acid (AMPS) and 2-hydroxyethyl methacrylate (HEMA) crosslinked by poly(ethylene glycol) dimethacrylate (PEGDMA) has been reported. They found proton conductivities of 0.02-0.11 S cm⁻¹ with significantly lower fuel permeabilities than that of Nafion (Fu et al. 2009). Sulfonic acid functionalized silica/PVA composite membranes have been reported, created by a sol-gel method, where -SO₃H groups were introduced by oxidation of -SH group present in mercaptopropylmethyldimethoxysilane (MPDMS) (Nagarale et al. 2004). The resulting membrane had good thermal and electrochemical properties. The phosphonic acid functionalized silica/PVA composite proton exchange membrane has also been reported. The phosphonic acid functionalisation was carried by phosphomethylation of aminopropyltriethoxysilane in aqueous medium. The resulting composite membrane had an excellent methanol barrier capability with good hydrophilicity and proton conductivity at higher temperatures. From selectivity parameter, they found, 50% silica loaded PVA composite with 3 h of phosphorylation resulted best protonexchange membrane. It was about 20% more suitability in comparison to Nafion 117 membrane for direct methanol fuel cell applications (Binsu et al. 2005). Apart from the silica composites, heteropolyacid and zirconium phosphate composite membranes have also been reported with good proton conductivity and lower methanol permeability.

Basic polymers can be doped with an amphoteric acid, which acts both as a donor and an acceptor in proton transfer and therefore allows for the proton migration. Phosphoric acid (H₃PO₄) doped polybenzimidazole (PBI) has received much attention in the past few years. The proton hopping from one N-H site to another contributes little to the conductivity, as pure PBI is not conducting. Proton hopping from one N-H site to phosphoric acid, anions contributes significantly to the conductivity. At a doping level of 2 mol H₃PO₄ per repeat unit, the conductivity of the membrane is about 2.5 x10⁻² S cm⁻¹ at 200 °C. The presence of the free or unbounded acid is necessary to improve the conductivity. At an acid-doping level of 5.7 mol H₃PO₄, the measured conductivity is 4.6×10^{-3} S cm⁻¹ at room temperature, 4.8×10^{-2} S cm⁻¹ at 170 °C, and 7.9 x 10⁻² S cm⁻¹ at 200 °C. However the ionic conductivities of PBI doped membranes could be further enhanced if it is doped with nanometric inorganic fillers. Though high acid doping levels result in higher conductivity, it deteriorates the mechanical properties of the acid doped polymer membranes, especially at temperatures above 100°C. This has been a critical issue for development of the acid doped polymer membranes. The use of thermally stable polymers like PBI allows for good mechanical strength at reasonably high acid doping levels. Further introduction of inorganic solid components into the polymer is expected to improve the mechanical behavior as well as the thermal stability, water adsorption and other properties. He et.al reported the PBI based ZrP nanocomposite membranes. It is known that ZrP is a surface proton conductor, the surface area and its

capacity for surface adsorption have a significant effect on the conductivity. For the acid doped ZrP/PBI membrane, there is a large variety of hydrogen bonding around each particle of ZrP, involving H₃O⁺, PO₄, H₂O, P-O and P-OH groups. The fine ZrP particles in the membrane therefore attract the protonated active ions or groups associated with the proton transfer, which might cause an improvement in the conductivity. The ZrP incorporated PBI membranes exhibited high ionic conductivity around 0.10 S cm⁻¹ even at 200°C. It also exhibited prompt ionic conductivity even at lower relative humidities. From this it is clear that included nanoparticles played a decisive role in the determination of ions transportation *via* their additional ion sites and strong water adsorption tendencies (He et al. 2003). The significant efforts which have been made on the polymer nanocomposite membranes and its important properties are given in Table 2.

6.4 Miscellaneous nanocomposite membranes

Apart from the normal blending techniques, efforts have been made on the irradiated membranes to identify the impact of nanocomposite technology. Gnanakumar et al. (2010) doped tin oxide particles with the PVdF-HFP copolymer before the grafting reaction. In course of finding, included nanoparticles reduced the polymeric content volume which has been available for the irradiation technique and decreased the grafting degree value and there by acidification degree value. In general, water adsorption is directly proportional to the acidification degree values. But a different trend was followed by the prepared nanocomposite membrane. Though the acidification values are lower, inclusion of hygroscopic fillers induces higher amount of water adsorption.

It has been reported that the hydrated tin oxide particles exhibit structural, bonded, and adsorbed water molecules. The structural, bonded, and adsorbed water molecules represent the condensed hydroxyl groups, hydrogen bonded water, and physisorbed water molecules, respectively. The structural and adsorbed water molecules are stored inside the micro-pores of tin oxide particles and are not released even at the higher temperatures. The adsorbed water molecules influence the ion transportation of the membrane. This suggests that the ionic conductivity is not only proportional to the number of attached acid molecules and also relates with the number of sorbed water molecules which act as proton sources and ion conduction paths. Though high ionic conductivity was achieved for the tin oxide included membrane, methanol permeability was much inferior to the bare PVdF-HFP membrane and attributed to the tortuous nature of the included tin oxide particles. Thus by the aforementioned efforts, PVdF-HFP-PSSA-SnO₂ membrane exhibited higher direct methanol performance than that of bare PVdF-HFP membrane (Gnana Kumar et al. 2010). Shen et al. reported the influence of nanometric alumina on the irradiated PVdF-PSSA membrane and the impact of nanocomposite technology has been clearly understood (Shen et al. 2006).

7. Future prospectives

The new nanoscale fillers has been a major contributor to the rapid development of polymer nanocomposites, robust structure-property-processing relationships with the polymers are critical to further market infiltration. Though the development of polymer nanocomposite membrane for fuel cell applications has been well developed, a specific nanoscale filler (or fillers), and a particular spatial arrangement of the filler are still in their infancy stage. The underlying mechanisms and compatibility between the nanofillers and polymers have to be clearly understood. It will bring forth a high durability of fuel cells.

Polymer	Nanofiller	Conductivity	Fuel cross over	Fuel cell performance	Reference
Nafion 117	—	90 - 120 mScm ⁻¹	14.1–17.2 cm ² s ⁻¹ at 60°C; 3.48 and 0.78 mol min ⁻¹ cm ⁻² (65 and 25°C, 1.5 M, and OCV)	50mA cm ⁻² (80°C and 1M)	Saarinen et al., 2007
Nation 115	—	41 – 61 mS cm ⁻¹	19.8 cm ² s ⁻¹ (25°C and 2M) & 4.66 mol min ⁻¹ cm ⁻² (25 °C and 1M)		Yang et al., 2001
Nafion®	SiO2		4 mol min ⁻¹ cm ⁻²	120mA cm ⁻² , 240mW cm ⁻²	Antonucciet al., 1999
Nafion®	ZrP	24–60 mS cm ⁻¹ (25 °C, 100% RH)		12 mA cm ⁻² (80°C and 1M)	Yang et al., 2001
Nafion®	Sulfonated CNT	0.01 S cm ⁻¹		260 mW cm ⁻²	Kannan et al., 2008
SPEEK	Silanes/silica	5 mS cm ⁻¹ (90 °C and 100% RH)	0.8×10 ¹⁶ m ³ m m ⁻² s ⁻¹ Pa ⁻¹		Ponce et al., 2004
SPEEK	SiO ₂ /ZrP/Zr-SPP	0.09 S cm ⁻¹			Bonnet et al., 2000
РВІ	ZrP + H ₃ PO ₄	9 x10 ⁻² S cm ⁻¹ at 200 °C, 5% RH			He et al., 2003
	SiWA + SiO ₂	2.2 10 ⁻³ 5cm ⁻¹ at 160 °C, 100% RH			Staiti et al., 2001
PVA/SSA	SiO ₂	10 ⁻³ to 10 ⁻² S cm ⁻¹	10 ⁻⁸ and 10 ⁻⁷ cm ² s ⁻¹		Kimet al., 2004
PVA/glycerin	ZrP+AA	10 ⁻³ to 10 ⁴ S cm ⁻¹ at 25 °C			Vaivars et al., 1999

Table 2. Summary of polymer nanocomposite membranes under development.

The cost of the nanoparticles and the environmental hazardous methods has to be decreased further. Nanoparticle synthesis *via* biological methods is an innovative field on now a days. A proper attention on the in-situ nanoparticle synthesis in the membranes *via* bio methods will bring a glory to this field.

Nanoscale multicomponent polymer blends is an innovative trend in the fuel cell field in which the nanoparticles should be arranged in between the two polymer layers. The nanoparticles embedded between the two polymeric layers may promote the thermal and mechanical behaviors and decreases fuel permeation of the membrane. In addition, new processing tools have to be developed to uniformly distribute nanofiller to produce homogeneous bulk properties or spatially vary the nanofiller concentration to meet specific design criteria.

Incorporation of nanometric metal(IV) phosphates such as zirconium phosphate (ZrP) and tin phosphate (SnP) in polymer matrices may result in an increased proton conductivity of the polymers. For this purpose, precipitation from a solution containing M(IV) ions, within an appropriate polymer matrix has to be carried out. With the appropriate amount of metal particles, appreciable degree of improvements in proton conductivity especially at high temperature and lower humidity fuel cell operation could be done.

By drawing inspiration from biology and engineered fiber reinforced composites, polymer nanocomposites with spatially controlled morphology are beginning to provide viable options to critical components of active devices. Polymer nanocomposites have recently become a part of established modern technologies, but the most significant accomplishments of these materials are still ahead of us. As an increasing number of scientists contribute to the understanding of polymer nanocomposites, what remains to be seen is which products will be critically enhanced and enabled by this broad and evolving class of materials.

8. Conclusion

Though we in the consumer society will have to live a technologically sophisticated version of the lifestyle currently practiced on the economic ladder, we have to hand over a pollution free environment to the next generation for their social and economical welfare. Fuel cells are the correct option for the above need. Many hurdles stand in the way of their ascendance however. Applications of PEMFC and DMFC have well developed but the recent development is polymer electrolyte membranes for the efficient fuel cell operation. Required parameters, commercially available membranes and its modifications, and recent trend towards the development of polymer nanocomposite electrolyte membranes have been reviewed in detail. Though the limitations of commercially available membranes have been cured to some extent so far, it has to overcome few more drawbacks. Improved, less expensive conducting materials now allow the newest fuel cells to work at higher temperatures, and generate more power per volume, both of which lower costs. The polymer nanocomposite membrane resulted in the enhanced thermal, mechanical, ionic condcutivity associated with the lower fuel drag than that of bare polymeric materials. The significant improvement has been achieved via the synergetic combination of organic and inorganic phases. Polymeric membranes applicable for fuel cells have been classified into various types such as perfluorinated, hydrocarbon and acid-base membranes. Irrespective of the aforementioned types, nanocomposite technology has been applied in all the aforementioned processes and make the polymer membrane suitable for fuel cell applications. According to the fuel cell experts, the commercialization of fuel cells is not far off. Both industrial and academic level activities should be triggered on the development of polymer nanocomposite electrolyte membranes to bring forth the commercialization of fuel cells one step ahead.

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Corrosion Behavior of Ni/Al₂O₃ and Ni/ZrO₂ Nanocomposite Thin Films

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1. Introduction

This paper investigates the effects of adding alumina and zirconia nanoparticles in the electrolyte bath on surface morphologies and structure of electrodeposited nickel, and their subsequent influence on the corrosion process in various solutions. These results are important for the fabrication of thermal and corrosion barriers by means of covering metallic surfaces with protective layers.

2. Nanocomposite preparation

The electrodeposition process and corrosion studies have been preformed on the same electrochemical cell. The corrosion process was monitored in a corrosion cell consisting of a round-bottomed flask, platinum auxiliary electrodes, and a standard calomel electrode serving as the reference electrode. The applied potential and resulting current were measured by a VOLTALAB 10 and 80 potentiostat/galvanostat and with a typical corrosion measurement software from RADIOMETER ANALYTICAL SAS Company. The general view of experimental arrangement is shown in figure 1. The temperature of the used solutions was controlled when placing the electrochemical cell in MLW U7 C thermostat.

On copper support, we have deposited 10 nanocomposite layers, in a nickel matrix, with ZrO_2 particles (6-8 nm) and 7 specimens having similar matrix with Al_2O_3 particles (20 nm) (Abreu et al., 2006; Yoo et al., 2006). We also created 3 specimens with simple nickel deposition in order to compare their behavior with the version with nanoparticles. The support specimens have been properly prepared for deposition, using specific solutions for degreasing, pickling and activation of surfaces. For the electrolyte solution, a Watt bath was used having the following features: NiSO₄·6H₂O-0.90M; NiCl₂·6H₂O-0.20M; H₃BO₃-0.28M; sodium dodecylsulphate [CH₃(CH₂)₁₁OSO₃Na]-0.4 g/l (Viswanathan et al., 2006). The pH value of the solution was maintained at 4.2 – 4.5 and the corrections were made using an acidic solution. The concentration of zirconia was 10 g/l and concentration of alumina varied from 0 to 20 g/L. Both types of nanoparticles were kept in suspension by a magnetic stirrer. The stirring rate of the plate agitator was 700 rpm. Firstly, the supports are decreased for 15-20 minutes in a solution and then wiped with a filter paper. Secondly, the specimen is introduced in the pickling solution (HNO₃ 20%) and thoroughly rinsed distilled water. We



Fig. 1. Equipment Voltalab 10 for electrodepositions and some corrosion measurements

noticed that the surface shows metallic lustre and the wash with distilled water creates a uniform film. Thirdly, the specimen is introduced in an activating solution ($H_2SO_450\%$) and washed again with distilled water. Finally, it is rapidly introduced in the electrolysis bath containing the prepared electrolyte solution. Before weighting them on a precision balance, the specimens need to be thoroughly dried. Depositions were made at an optimal temperature of 40° C for 90 minutes and a current density of 2A/dm². The cathode consisted of the working specimen and the anode consisted of pure nickel with the same surface area as the specimen. After 90 minutes, the electric power was disconnected and electrodes were removed from the bath. The specimens with composite deposition were washed with plenty of distilled water. After the specimens dries, they are weighed on the precision balance to compute the actual deposited quantity.

The main tools used for the surface characterization for nanocomposite layers were scanning electron microscopy (SEM) equipped with an EDAX, and X-ray diffractometer (XRD). The OLYMPUS PM3 microscope allows for morphological observations of the microstructure. The analysis by XRD shows that only some planes common to nickel system are expected and these are presented in Table 1.

(hkl)	20 (°)	I (a.u.)
111	44.51	100
200	51.85	42
220	76.37	21
311	92.94	20

Table 1. Planes of nickel system

3. Structural analysis

The obtained electrodeposited layers of nickel having alumina or zirconia nanoparticles were studied by scanning electron microscopy at different magnifications. It is important to choose the optimal magnifications to obtain the best images in which some agglomeration of nanoparticles in the electrodeposited layers can be observed.

If a cross section is made in the resulted nanomaterial, it is possible to observe different thicknesses of the electrodeposited layer. This thickness depends of current density, the deposited time and other variable of electrodeposition process (e.g. nanoparticles composition). The effect of nanoparticles on thickness can be explained by the growth of the agglomerating particles in the layers that become bigger when higher amounts of particles are present (Leng et al., 2006).

In figure 2 SEM images of Ni/Al_2O_3 electrodeposition are displayed for five different alumina nanoparticles concentrations reaching to 100g/l.



Fig. 2. SEM images of Ni/Al₂O₃

As alumina was added to the electrolyte in increasing concentrations, a general refinement in the grain structure on the surface is observed. With addition of 5 g/l of alumina, the average size of the pyramids on the surface is clearly reduced (Gheorghies et al., 2006). There is also a reduction in the surface grain size to micrometer and sub micrometer grains. These results show that the surface morphology is greatly refined by the presence of alumina in the bath for the coatings deposited at 2 A.dm⁻².

The chemical analysis of electrodeposited layer with alumina nanoparticles has been estimated by EDAX method. The typical spectrum showing the chemical construction is presented in figure 3.



Fig. 3. EDAX spectrum of electrodeposited film with alumina nanoparticles

X-ray pattern from an electrodeposited film of nickel having a concentration of 10 % alumina nanoparticles in figure 4 is presented. Although EDAX spectra pointed out aluminum, only the characteristic peaks of nickel can be observed.



Fig. 4. X-ray diffraction pattern of electrodeposited nickel film with 10 % alumina nanoparticles

The thin films of nickel which were obtained with zirconia nanoparticles present in the electrolyte had an uniform white-silvery appearance. To obtain a reference for the determination of deposition efficiency, three pure nickel depositions were first conducted. In theory, there should have been deposited 8.21g/dm², while experiments showed a

deposit of 7.8241g/dm². Nickel weight deposited on the specimen was $m_{experimental} = 0.3129$ g and $m_{theoretical} = 0.3284$ g. Achieved efficiency was $\eta = 95.30$ % i.e. an optimum deposition efficiency over 95%, typical for nickel depositions in an electrolytic bath of sulfate-chloride; in a Watt's bath, 97.5% efficiency is obtained. Average weight of nickel with ZrO₂ deposited on the specimen is $m_{experimental} = 0.2822$ g. From $m_{theoretical}$ and $m_{experimental}$, efficiency can be deduced as $\eta = 85.94$ %.

Pure nickel depositions were obtained with an efficiency of more than 95.30%. On the other hand, in the experiments performed for composite depositions, a smaller efficiency was achieved due to the presence of ZrO₂ particles. One possible explanation is that in the paths followed by the Ni²⁺ ions to the cathode and that of the anions to the anode, ZrO₂ particles in the suspension may slow the nickel reduction process. Moreover, ZrO₂ particles can be found in the deposits, and there is an equilibrium between the forces keeping the particles down in the deposition and those existing in the suspension. This situation is not yet fully understood for a composite deposition mechanism.

4. Corrosion tests

Corrosion tests have been performed for composite coating specimens of Ni /ZrO₂ in three different types of solvents: NaCl 3%, Na₂SO₄ 0.1M and H₂SO₄ 0.1N. The results were compared with depositions of metallurgical nickel. The Na₂SO₄ 0.1 M solution is an electrolyte who has the advantage of being inert over most of the other tested materials, and the 0.1 M concentration ensures the appropriate conductivity for the three electrochemical studies that were performed: polarization curve, EIS spectroscopic impedance, and Mott-Schottky spectroscopic impedance (Yoo et al., 2006).

Previously, we isolated with nylon (polytetrafluoroethylene) the surface not subjected to electrochemical tests. Out of the deposited coating (Ni/ZrO₂) area of 4 cm², an area of 0.5–1cm² was reserved for the electrochemical experiments, polarization curves and spectroscopic impedance.

The electrochemical cell used for the electrochemical tests consisted of a glass recipient with a cap having a series of apertures through which we inserted the solution to be analyzed, the working electrode [deposition specimen obtained on the copper support], the auxiliary electrode [helical platinum (Pt) wire] and the referential electrode [horn mercury electrode Hg/HgCl_{2sat}. ($\epsilon = 0.234$ V)]. The solution was stirred by introducing a small magnet covered by a nylon or glass layer, which was then moved a magnetic stirrer.

Nickel specimens with zirconium oxide particles have been studied against pure nickel specimens. Initially, polarization curves were achieved in the previously mentioned electrolyte solutions (NaCl 3%, Na₂SO₄ 0.1M and H₂SO₄ 0.1N). Then we observed the behavior of the Ni/ZrO₂ depositions and that of the metallurgical nickel specimen.

The working circuit consisted of: referential electrode: horn mercury, auxiliary electrode: platinum and working electrode: deposition in nickel matrix. This circuit was connected to a computer which recorded the experimental data. The polarization curves i = f (E) were obtained in the following conditions: voltage 0: -500 mV; voltage 1: +500 mV; voltage 2: +1000 mV; sweeping speed (rate) v = 150 mV/min; number of cycles: 1, minimum current: -50 mA and maximum current: +50 mA. Figures 5-7 contain these polarization curves, and the corresponding numerical values are are synthetically reported in Table 2.

	Ni	Ni/ZrO ₂	Ni	Ni/ZrO ₂	Ni	Ni/ZrO ₂
	Na ₂ SO ₄ 0.1 M		NaCl 3%		H ₂ SO ₄ 0.1 N	
E (i=0) (mV)	-321.1	-131.3	-237.1	-232.2	-257.9	-257.9
$\mathbf{R}_{\mathbf{p}}$ (k Ω ·cm ²)	16.41	104.54	7.85	20.98	126.63	126.63
i _{cor} (μA/cm²)	0.9583	0.0693	1.299	0.229	0.0909	0.0909
\mathbf{v}_{cor} (mm/year)	0.013	0.001	0.018	0.003	1.243	1.243
A (cm ²)	7.9	0.6	8.69	0.72	8.69	0.54

Table 2. Experimental data obtained from Polarization curves Key: E – voltage; i_{cor} – corrosion intensity; R_p – polarization resistance; v_{cor} – corrosion rate; A – surface area



Fig. 5. Polarization curves: a) Ni in NaCl 3% solution, b) Ni/ZrO₂ in NaCl 3% solution



Fig. 6. Polarization curve: a) Ni in $\rm Na_2SO_4$ 0.1 M solution, b) $\rm Ni/ZrO_2$ in $\rm Na_2SO_4$ 0.1 M solution



Fig. 7. Polarization curve Ni in H₂SO₄ 0.1 N solution, b) Ni/ZrO₂ in H₂SO₄ 0.1 N solution

The obtained curves and the rates of corrosion indicate that the voltage is shifted to higher positive values for composite coatings of Ni/ZrO₂ (-232.2 mV for NaCl 3% solution; -131.3 mV for Na₂SO₄ 0.1M solution) against the metallurgical nickel (-237.1 mV for NaCl 3% solution; -321.1 mV for Na₂SO₄ 0.1M solution) and against the initial voltage, – 500 mV. In H₂SO₄ 0.1N solution, the voltage is found as being the same (-257.9 mV). The highest positive potential (-131.3 mV) was obtained for composite coatings of Ni/ZrO₂ in Na₂SO₄ 0.1M solution. A significant decrease in voltage occurs for the Ni/ZrO₂ specimens in Na₂SO₄ 0.1 M electrolyte, of approximately 200mV decrease. For the other electrolytes, no signification changes between the composite depositions and pure Ni were recorded.

The highest change in polarization resistance compared with pure Ni is obtained for Ni/ZrO₂ composite deposition in a Na₂SO₄ 0.1 M electrolyte. Correlated with this parameter, the corrosion intensity is the lowest on the same specimens, respectively 0.0693 (μ A/cm²) for a polarization resistance of 104.54 (Kohm·cm²). The higher corrosion resistance and smaller the corrosion intensity are, the more resistant is the specimen to the destruction process.

In table 3 the corrosion rates are listed, expressed in mm/year. The lowest value was obtained for Ni/ZrO_2 composite deposition in Na_2SO_4 0.1 M electrolyte (0.001 mm/year) and the second lowest one for NaCl 3% (0.003 mm/year).

t (min.)	10	45	60	70	85	90	120	140
E (V)	0.18	0.15	0.15	0.15	0.14	0.13	0.11	0.1
t (min.)	180	200	240	1440	2670	2735	2790	2820
E (V)	0.09	0.09	0.08	0.09	0.1	0.09	0.02	0

Table 3. Experimental data on Spectroscopic Impedance research

In the H₂SO₄ 0.1 N electrolyte, which is highly acidic, the parameters for specimens studied by comparison are identical, thus polarization curve research in this electrolyte does not provide analytical information.

In conclusion, the determination of the polarization curve must be performed in a proper electrolyte, to maximize the amount of information useful for research. For the studied specimens it was proved that Na₂SO₄, which is an inert electrolyte which resulted from a

tough acid and a tough base, is the most appropriate for the study of polarization curves. Ni/ZrO_2 composite deposition specimens show significantly improved parameters (R_p and i_{cor}) compared with metallurgical Ni.

In figure 8, the overlapping of two polarization curves is shown: Ni/ZrO₂ in Na₂SO₄ 0.1 M solution and Ni/ZrO₂ in NaCl 3% solution. The two curves cross at: on voltage E ϵ (-300 mV, -200 mV) and a corrosion rate i_{corr} = 0 μ A/cm².



Fig. 8. Polarization curves – Overlapping: Ni/ ZrO_2 in Na₂SO₄ 0.1 M solution (1), Ni/ ZrO_2 in NaCl 3% solution (2)

In figure 9, the polarization curve is shown for nickel and Ni/ZrO₂ specimens in H₂SO₄ 0.1 N solution. The curve for nickel has a maximum peak at a voltage E ϵ (7mV, 14 mV) and a corrosion rate $i_{corr} \epsilon$ (2.150 μ A/cm², 2.154 μ A/cm²). For Ni/ZrO₂ two maximum peaks are present at a voltage E₁ ϵ (-65 mV, -55 mV), a corrosion rate $i_{cor 1} \epsilon$ (4 μ A/cm², 4.2 μ A/cm²), and at a voltage E₂ ϵ (80 mV, 100 mV), with a corrosion rate $i_{cor 2} \epsilon$ (2.3 μ A/cm², 2.5 μ A/cm²). In addition, we juxtaposed the polarization curbes for Ni/ZrO₂ in H₂SO₄ 0.1 N solution (1), and Ni in H₂SO₄ 0.1 N solution (2). Both curves have a peak in the same voltage range: E ϵ (-255 mV, 200 mV).



Fig. 9. Polarization curves: Ni/ZrO₂ in H_2SO_4 0.1 N solution (1), Ni in H_2SO_4 0.1 N solution (2) – Overlapping

For composite coatings like nickel – zirconium oxide, compared to nickel coatings, polarization curves have almost the same rates, but shifted to an increased voltage, proving that these composite coatings have better resistance to corrosion.

The corrosion protection can be attributed to the presence of ZrO_2 particles in nickel matrix, because their presence on the metal surface creates a barrier for oxygen reduction. In solutions, the composites are not stable. It is possible to selectively dissolve the metallic matrix or the disperse phase or both (matrix-disperse phase).

Corrosion processes are essentially electrochemical nature processes and voltage and current parameters can be accurately measured with modern equipment. For the corrosion study, polarization resistances can be evaluated from spectro-electrochemical impedance data (EIS) in a large frequency range ($10^5 - 10^{-3}$ Hz). A voltage change indicates a corresponding change of intermediate species concentration.

The spectroscopic impedance measurements were performed on composite specimens, nickel with zirconium oxide (Ni/ZrO₂) particles in Na₂SO₄ solution, as working electrolyte for the electro-chemical cell. This way, the behavior of the layer deposited in the electrolytic solution was traced during a period of time, to evaluate the parameters.

The working equipment contains a two component circuits: the main and secondary circuits. The main circuit consists of: referential electrode: horn mercury (connected to white color); auxiliary electrode: platinum (connected to red and orange colors) and working electrode: specimen (connected to green and blue colors). The secondary circuit is realized by a salt bridge connecting the referential electrode to the working electrode (Hamann et al., 1998). The salt bridge prevents contamination of saturated KCl solution from the horn mercury electrode with impurities coming from the solution to be analyzed. To measure the voltage in horn mercury, a voltmeter was introduced in the circuit, with a lug to referential electrode and one to the working one. This circuit is connected to computer and data for electrochemical analysis are recorded.

Specimens undertaking the experiments have been evaluated for certain time spans. The value of voltmeter-measured voltage is reported during the entire electrochemical analysis. Results are rendered in table 3, and diagram E= f(t) is rendered in figure 11. From the spectroscopic impedance measurements, an evaluation can be made by comparing the differences between the measuring voltage values depending on time, as presented in table 3. The voltages can provide insight into the strength of the coating.

From figure 10 shows that voltage changes with time, and a constant voltage drop is recorded from 180 mV to 0 mV during 47 hours. Additional data is presented in figures 11-



Fig. 10. Voltage variation on time

12, rendered as Bode and Nyquist charts. Bode chart is usually useful to physicists, while Nyquist chart is preferred by chemists. The impedance measurements on various frequencies can provide full information on the electrochemical system, which gives a particular value to this technique (Hamann et al., 1998; Rusu et al. 2010).




Fig. 11. Representation of Impedance Spectroscopy (BODE Diagram) for the experimental system of Ni/ZrO_2 in Na_2SO_4 0.1 M solution at t = 0 s(a), 1h(b), 2 hrs(c), 3h(d), 4 hrs(e), 24h(f), 46 hrs(g), 47(h)

Figure 12 shows that Ni/ZrO₂ composite system has a high polarization resistance, with a maximum of 40 Kohm for a high frequency. After 46 hours Nyquiest diagram shows a small 300 ohm polarization resistance, and a small decrease of polarization resistance with time. This suggests that the presence of zirconium oxide in the deposition may cause load transfer, since this substance can act as activator for the cathode reduction process of the metal.

A specimen of Ni/ZrO₂ composite deposition was subjected to Mott Schottky approach, which is a variant of Spectroscopic Impedance. In this approach, behavior of voltage depending resistance and capacity is traced. The data we obtained is plotted in figures 13-15. At a voltage of ~100 mV the specimen has a high polarization resistance and the capacity is at a minimum of 0 mV, which explains the good properties of the specimen in the 0-100 mV range, and its corrosion resistance on higher voltages. The capacity decreases for the interval: E ϵ (-500 mV, 0 mV) and then increases for the interval E ϵ (0 mV, 500 mV).





Fig. 12. Representation of Impedance Spectroscopy (Nyquist diagram) for the experimental system of Ni/ZrO_2 in Na_2SO_4 0.1 M solution at t = 0 s (a), 1h(b), 2 hrs(c), 3hrs(d), 4 hrs(e), 24hrs (f), 46 hrs(g), 47hrs(h)



Fig. 13. Variation of capacity (1) and resistance (2) of nanocomposite thin films versus applied potential



Fig. 14. Polarization curve (1) and variation of resistance (2) of nanocomposite thin films

Our experiments have shown that the Ni/ZrO_2 composite coatings resist better to corrosion, compared to metallurgical nickel depositions. The best corrosion protection is obtained when the layers have low capacity. The layer is less active, therefore more resistant to corrosion.

The specimens subjected to electrochemical studies were washed with plenty of distilled water and dried, and the raylon was subsequently removed from the coated surface (Rieger,

1994; Thiemig et al. 2009). The specimens can be inspected with an electronic microscope to view potential alterations of the surface to be studied.



Fig. 15. Polarization curve (1) and variation of capacity (2) of nanocomposite thin films

5. Conclusions

This paper deals with the electrochemical preparation and study of Ni/Al_2O_3 and Ni/ZrO_2 nanocomposite thin layers on Inconel or cooper substratum. The comparison between the properties of composite coatings and metallurgical nickel coatings yielded conclusive results. Electrochemical processes offer an alternative way for obtaining composite coatings with unique properties, superior to those of constituent materials.

More than that, the composite coatings can be obtained using affordable processes which offer precise control on its parameters. We determined the most relevant factors for the success of composite coatings with directed composition are the nature of constituents, and electrolyte and electrolysis conditions. For example, the chemical and physical reactions of Ni/ZrO₂ composite plating depend on the electrolyte, for each test solution used.

The study of polarization curves and electrochemical impedance offers useful information on the kinetics of chemical reactions on the electrode. The corrosion voltage has higher values for composite coatings of Ni/ZrO₂ in Na₂SO₄ 0.1 M solution, which is the most appropriate solution for studying the polarization curves. The 0.1 M Na₂SO₄ concentration has an appropriate conductivity for performing electrochemical tests.

The physical and chemical properties (hardness, stability, wear and chemical resistance) of composite coatings are superior to those obtained by conventional procedures and recommend their usage in electronics, medicine, engineering and anti-corrosion protection.

Alumina and zirconia composite electrodepositions were done in a nickel matrix, and the result exhibited higher corrosion resistance than that of pure nickel.

Additions of alumina nanoparticles with a particle size of 20 nm of 5 g/l and 10 g/l into nickel plating bath change the preferred growth direction of the electrodeposited nickel from <100> to <111>.

When alumina is added, the microstructure of nanocomposite coatings is different from that obtained using pure nickel. Moreover, deposition of zirconia in nickel metallic matrix improves anti-corrosion protection of layers.

The obtained results are promising for developing new corrosion-resistant materials. They suggest that metal oxide nanoparticles coatings can be an effective option for surface protection, as it introduces a barrier against aggressive environment and metallic sub-layer. This approach is relatively new and warrants further research into the mechanisms that cause nickel-metal oxide composite coatings to improve corrosion resistance.

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Part 3

Carbon Nanotube

A Fabrication Process of Composite Micro Components using Super Fine Stainless Steel and Ceramic Nano Powders

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1. Introduction

Fabrication of micro components from different monolithic materials such as ceramics, metals, and polymers have been discussed before [Jun et al., 2008; Mohamed et al., 2008; Bong-Kee & Tai, 2008], but hardly any research has been reported in fabrication of composite microparts [Ping et al., 2008; Hany & Kyle, 2009; Su-Jin et al., 2008]. This chapter introduces a novel approach to fabricate stainless steel ceramic composite micro machine components. The two types of composites to be introduced are stainless steel-alumina and stainless steel-titania. Three types of powders were tested, including 5 µm stainless steel, 400 nm alumina and 320 nm titania. Four different compositions prepared for each composite type are 2.5, 5, 7.5 and 10% weight of ceramic. Characterization of composite micro components in terms of slurry preparation process, sintering conditions, shape retention, density, linear shrinkage and micro hardness is reported in detail. The fabrication process is divided into three stages. In the first stage, SU-8 master moulds and their negative replica soft moulds are produced using softlithography process. The second stage includes preparation of composite slurries, filling soft micro moulds and obtaining composite green micro components. In the third stage, the composite green micro components are de-bound and sintered in vacuum and nitrogen-hydrogen mixture (90% nitrogen and 10% hydrogen) respectively at 1350 °C. Afterwards, the properties of sintered micro components are studied in detail.

2. Experiments

2.1 Preparing SU-8 and soft moulds

SU-8 2075 [MicroChem, USA] was used for fabricating 1mm thick master moulds of micro gears, pistons and linkage rods. The SU-8 fabrication procedure are as follows: (i) casting SU-8 resist onto 4 inch Silicon wafer and soft baking at 65C° for 2 hours followed by 95C° for 34 hours; (ii) exposing the coated wafer in Canon PLA-501 FA UV-mask aligner; (iii) post

exposure baking at 65C° for 5 minutes followed by 95C° for 15 minutes; (iv) developing the wafer in EC solvent. After SU-8 master moulds were produced, they were replicated into PDMS soft moulds. Figure 1 shows high quality SU-8 master moulds and their negative soft moulds replicated from the master moulds. Details of the fabrication of SU-8 and replication of soft mould can be found in [Mohamed et al., 2008].



Fig. 1. SEM images of (a) SU-8 master moulds and (b) negative replicas soft moulds.

2.2 Preparing composite slurry and obtaining green components

5 µm 316-L Stainless steel powder with composition of 65.5%Fe, 18.5%Cr, 11.6%Ni, 2.3%Mo, 1.4% Mn and other minor elements (Sandvik Osprey UK) is used as the matrix material. The alumina powder used in this research is α -alumina (≤ 400 nm) with 99.9% metal base, supplied by Alfa Aesar UK. The titania powder has an average particle size of less than 320 nm, supplied by Huntsman England, UK. Duramax B-000 in combination with B-007 and D-3005 were used both as a binder and as a dispersant in the process. Duramax B1000 and B1007 are aqueous emulsion used as a binder in the ceramic fabrications [Mohamed et al., 2008; Dou et al., 2003; Zhigang et al., 2007]. D-3005 is an ammonium salt of acrylic homopolymer which was used for dispersing various types of powders. Different composite compositions were prepared containing 2.5, 5, 7.5 and 10% alumina by weight. In order to prepare composite slurries, a new approach is used to homogenize the ceramic nano particles into stainless steel micro powders as follows: (i) dispersing both stainless steel and ceramic powders in two separated specimen tubes by mixing dispersant, distilled water and powder together, (ii) mixing the two dispersed slurries together, adding the binder and mixing well, (iii) filling the soft mould and obtaining the green parts. Figures 2 (a) and (b) show the composite green micro components based on alumina and titania nano particles, respectively, which retain the same quality of the SU-8 master moulds.



Fig. 2. SEM images of the composite green micro components based on: (a) 10% alumina and (b) 10% titania.

3. De-binding and sintering

The composite green parts were de-bound in nitrogen atmosphere and then sintered in vacuum and forming gas of 90% nitrogen and 10% hydrogen in separate experiments at 1350 °C.

4. Results and discussion

After sintering, the composite micro components sintered in forming gas and vacuum were inspected under SEM and shown in Figure 3 (a) and (b), respectively. It is found that all micro features are retained after sintering. The geometric quality of the sintered composite micro components based on titania is the same as that based on alumina. Generally, ceramic inclusions are distributed homogenously throughout the stainless steel matrix after sintering. Analysis were carried out on the effects of composite compositions on both green and sintered densities (based on stainless steel, 8g/ml), linear shrinkage (based on micro gear diameter and SU-8 is used as reference) and micro hardness (Vickers) of sintered composite micro components and the analytical plots are provided in Figures 4 (a), (b), (c) and (d). As expected, the green and sintered densities decrease with the increase of ceramic content. Because the density of the alumina is lower than that of the stainless steel, increasing its content decreases the overall composite density. The linear shrinkage curves follow the same trend as the sintering density curve, in which the greater the ceramic contents are, the lower the linear shrinkage and vice versa. Moreover, the more the ceramic content increases, the higher the hardness of different ceramics in different sintering atmospheres. It is also clear that, for given composite composition and sintering atmosphere, the hardness of the micro composites based on alumina powder is greater than

that based on titania one. This happens due to the greater hardness of pure alumina than that of pure titania. Furthermore, for a given composite composition and ceramic type, the hardness of the composites sintered in nitrogen/hydrogen mixture atmosphere is significantly greater than those sintered in vacuum. The hardness based on nitrogen/hydrogen mixture atmosphere may increase due to one of the following reasons: (i) because nitrogen/hydrogen mixture contains 90% of nitrogen, it may form nitride precipitating into the grain boundaries and harden the stainless steel micro components [Monnapas et al., 2008]; and (ii) it may be dissolved into the grains and promotes solid solution hardening [Abenojar et al., 2003].



Fig. 3. SEM images of stainless steel ceramic composite micro components: (a) based on10% alumina and sintered in nitrogen/hydrogen mixture, and (b) based on10% titania and sintered in vacuum.

5. Conclusions

This chapter proposes a novel approach to fabricate stainless steel composite micro components based on experiments. In the research, composite micro components were successfully fabricated from stainless steel alumina and stainless steel titania with different compositions. The fabrication process was investigated in detail and characterizations of composite micro components were studied in terms of composite preparation process, green and sintering density, linear shrinkage, and micro hardness. The following conclusions can be drawn from the research:

- 1. Increase the ceramic content decreases both density and linear shrinkage, but it increases the hardness.
- 2. For a given composite composition, using nitrogen/hydrogen mixture and vacuum atmospheres produces nearly the same density and linear shrinkage, while the hardness increases significantly by using nitrogen/hydrogen mixture atmosphere.
- 3. For a given composite composition, the sintered density and linear shrinkage of stainless steel-titania composite is greater than stainless steel-alumina, while the hardness of the later is greater than the former one.



Fig. 4. Effect of ceramic inclusion on: (a) composite green density, (b) composite sintered density, (c) composite linear shrinkage and (d) composite Vickers hardness.

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Nanowire-Polymer Nanocomposites as Thermal Interface Material

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1. Introduction

Packaging of semiconductor electronic device is a challenge due to the progressive increase in the power level of operating devices which is associated with the increasing device performance. As semiconductor device feature sizes continue to be reduced, ensuring reliable operation has become a growing challenge. The effective transfer of heat from an integrated circuit (IC) and its heat spreader to a heat sink is a vital step in meeting this challenge. The ITRS projected power density and junction-to-ambient thermal resistance for high-performance chips at the 14 nm generation are >100 Wcm⁻² and <0.2 °CW⁻¹, respectively. The main bottlenecks in reducing the junction-to-ambient thermal resistance are the thermal resistances of the thermal interface material (TIM) (Prasher 2006) and the heat sink. The primary goal of this chapter is to review the metallic-nanowire nanocomposites as thermal interface material compared to other types of thermal interface materials. The first section of the chapter will review different types of nanowire-polymer composites as well as carbon nanotube-polymer composites as thermal interface material. In recent years, carbon nanotube (CNT) and nanotube-polymer composites were proposed in many publications as a possible TIM with high thermal conductivity and low thermal impedance. However, the possibility of inadvertently incorporating contaminating impurities, the existence of voids between CNTs, and the growth conditions of CNT arrays greatly affect the effective thermal conductivity of CNTs, typically resulting in a TIM with a large performance uncertainty. On the other hand, nanowire-polymer nanocomposites can be proposed as thermal interface material where due to the inclusion of nanowires, composites should achieve high thermal conductivity. The later sections of this chapter will describe the research and development ongoing in the area of nanowire-polymer nanocomposites. The fabrication routes for the nanowires and the nanowire-polymer composites as well as the characterizations of the nanocomposites will be discussed in detail. The applicability of metallic nanowire-polymer nanocomposites as thermal interface material will be evaluated.

2. Thermal interface materials

When two nominally flat and smooth solid surfaces are joining together to form a dry joint (Xu 2006) as can be seen in Fig. 1(a), roughnesses on both surfaces limit the actual area of

contact between the two solids to a small percentage (about 1%-2%) of the apparent contact area (Greenwood and Williamson 1966). Therefore, the heat flux through this interface - if neglecting the heat transfer by radiation between the surfaces - flows by two different heat conduction paths: firstly, solid-to-solid conduction through the contact points and secondly, conduction through the air (a poor thermal conductor compared to the solid materials) trapped between the area of non-contact. Those two different heat transfer paths constrict the heat in a confined area: this limiting factor has been called thermal contact impedance. In order to diminish the thermal contact impedance and consequently increase the heat transfer rate, the air gap formed by the mating surfaces must be replaced by a material with a higher thermal conductivity than that of the air: those materials are commonly called TIMs. From Fig. 1(b), the total thermal impedance due to the TIM insertion (θ_{TIM}) between the two mating surfaces can be retrieved as follows (Prasher 2001):

$$\theta_{\text{TIM}} = \frac{\text{BLT}}{\text{k}_{\text{TIM}}} + \theta_{c1} + \theta_{c2} \tag{1}$$

where θ_{c1} and θ_{c2} represent the contact impedances of the TIM with the two bounding surfaces, k_{TIM} is the thermal conductivity of the TIM and BLT is its bond line thickness. Since the main objective of thermal management in electronic packaging is the efficient removal of heat from the semiconducting device to the ambient, the total thermal impedance from the junction-to-ambient (θ_{ja}) has to be minimized: the lower the thermal impedance, the lower the temperature drop from the silicon die to the ambient.



Fig. 1. Sketch showing the real area of contact of a joint formed by two rough surfaces (a); sketch representing a TIM in the real application scenario (b) (Prasher 2006).



A Contact impedances	θ - Junction-to-case	 T_j - Junction
$\theta_{c1,c2,c3,c4}$ = Bulk impedance of TIM1.2	Θ_{ic} - Junction to cace	ο Τ _c - Case
θ_{track} - Heat sink	θ - Case-to-sink	• T _s - Sink
θ_{Hs} - Heat spreader	θ., - Sink-to-ambient	• T _a - Ambient
	30	

Fig. 2. (a-b) shows two sketches of a microprocessor package assembly used in a real application scenario of electronics cooling, respectively for past and more recent desktop applications. Here, the superimposition of different layers of materials in order to build the assembly leads to a creation of a thermal impedance chain as shown in Fig. 2(c-d) (Chiu 2006; Mahajan 2002; Prasher 2006; Sauciuc et al. 2005; Torresola et al. 2005; Xu 2006).

For convenience, by looking only at the sketches in Fig. 2(b) and (d), the heat transfer through the complete assembly involves the following three major stages (along with the respective thermal impedances) (Grujicic et al. 2005):

- Heat transfer within the device package (θ_{ic}).
- Heat transfer from the package to a heat sink (θcs).
- Heat transfer from the heat sink to the ambient environment (θ sa).

The main bottlenecks in reducing the θ_{ja} are the interfacial impedances between the package and the heat sink (Prasher 2006): this is due to the mating surfaces between the package and the heat sink, which, in the real application scenario, are generally neither fully conforming nor smooth and thus, leading to a significant increment of thermal contact impedance. Hence, the thermal management within the area of the chip is a relevant issue: Table 1 summarizes the ongoing challenges related to air cooling technology in order to minimize the junction-to-case thermal impedance.

Thermal impedance	Thermal management challenge		
Junction-to-case	IC-level cooling		
	Package architecture development		
	Interface thermal contact impedance minimization		
Case-to-heat sink	Interface thermal contact and TIM bulk impedance		
	Minimization		
Heat sink-to-ambient	Advanced heat sink manufacturing technologies		
	Improvement of heat spreading technologies		
	Integration of hybrid cooling solutions		
	Aerodynamic fan performance improvement		
	Airflow optimization		
	Heat sink surface fouling minimization		
	Sustainability		

Table 1. Air-cooling solutions: thermal management key areas for improving the heat removal from the silicon die to the heat sink (Rodgers et al. 2005). The highlighted text shows the topic on which this study is focused.

In relation to this chapter, the research presented will focus on the case-to-heat sink impedance, in particular by looking at the thermal properties of TIMs and the way to accurately quantify the same. To this end, the following section reviews the recent progress of the research and industry work performed to develop new emerging materials and improve the existing state-of-the-art; furthermore, a variety of methods and their implementations used to characterize the TIMs are also introduced.

3. Review of nanowire/ nanotube based composites

Polymer nanocomposites can have potential microelectronic applications in a wide range of areas which includes resistors, inductors, capacitors, lasers, low loss dielectric, waveguide, thermal interface materials, etc. Most of these nanocomposites used nanoparticles and micro particles as filler materials to tune the physical and electrical or thermo-mechanical properties. The use of nanowires or high aspect ratio structures are recently been investigated. The use of high aspect ratio structures has one obvious benefit and that is its ability to achieve low percolation threshold in a nanocomposite compared to nanoparticles.

The down side is the composite material may not be as flexible as the nanoparticle infused nanocomposites. Carbon nanotube (CNT) nanocomposites may be the exception where due to its ultra high aspect ratio the tubes are flexible enough and until a certain percentage of inclusion the nanocomposites made using CNT as filler can have similar flexibility and modulus as nanoparticle filled nanocomposites.

Micro-and nano-boron nitride (BN) particles, aluminium nitride, aluminium oxide, silver and other metals act as thermal conductor in either silicone or epoxy compounds. Btechcorp has patented a process for aligning fine (8 µm diameter) continuous metallic fibres (Ni, 40% vol.) through the thickness of a polymer matrix (Btechcorp 2008). Arctic Silver invented a commercially-available paste made of high-density filling of micronised Ag and enhanced thermally conductive ceramic particles dispersed in a proprietary mixture of advanced polysynthetic oils, claiming a thermal conductivity as high as 8 Wm⁻¹K⁻¹ (ArticSilver 2010). Kempers et al. developed and characterised a novel metal micro-textured (MMT) TIM consisting of a thin metal foil with engineered conical micro-scale features which deform under clamping pressure and thus, creating a continuous thermal path between the contacting surfaces (Kempers et al. 2009a; Kempers et al. 2009b). Carlberg et al. introduced and characterised the thermal performance of a nanostructured polymer-metal composite which consists of high-porosity nanofiber network infiltrated with a low melting temperature alloy (Carlberg et al. 2008a; Carlberg et al. 2008b; Carlberg et al. 2009). Wunderle et al. developed and applied different surface modification methods to create the so-called "nano-sponge" in a thin Au layer (Wunderle 2010). A second technology using Agpowder on Ag surface metallisation (sintering approach) has also been developed.

3.1 Nanotube composites

The urgent necessity of novel and high performance TIMs from the silicon devices companies has drawn the attention of researchers during the last decade (Liu et al. 2008a; Liu et al. 2008b). Therefore, TIMs based on carbon composition including CNTs, graphite; diamond and amorphous carbon are being studied among academic institutions and industry. The reason behind this is the great potential in term of thermal conductivity showed by the carbon allotropes (Melechko et al. 2005; Ngo et al. 2004). Worthwhile to mention research groups in the field of carbon-based TIM development are reported as follows: Purdue University are carrying on works on different methods of growing vertically aligned-CNTs along with new test approaches in developing the same (Cola et al. 2009; Cola et al. 2007a; Cola et al. 2007b; Xu and Fisher 2006). At Hong Kong University lift-off transfer of CNT films and development of Cu-CNT composite have been investigated (Chai et al. 2007a; Chai et al. 2007b; Chai et al. 2007c). At Tsinghua University CNT-PDMS (polydimethylsiloxane) composite by inject moulding has been invented (Huang et al. 2005). Also we have investigated different types of CNT-polymer to study the thermal properties of these nanocomposites (Razeeb et al. 2007; Xu et al. 2008).

Despite the great efforts put forward from the research, these new TIMs are unfortunately still far away from being available on the market because the performance exhibited is still not high enough to overtake the current best-in-class commercial products: this concept is also emphasised by the ITRS which predicts the earliest potential insertion of some cutting-edge materials for thermal management not sooner than 3-5 years. Many technical issues can be identified (Liu et al. 2008b). Theoretical predictions show that CNTs have extremely high thermal conductivity: these computations are mainly based on the assumption that

CNTs are ideal atomic structures, whereas in the real application scenario defects and impurities contribute to lowering their thermal conductivity. Furthermore, the contact thermal impedance between nanotubes and other substances, e.g. the polymer matrix in composites, is very high and even the functionalisation of CNTs is not sufficient to enhance consistently the performance of those composites. Also, CNTs have a high modulus of elasticity and when aligned in a vertical array, this may cause an increase in contact impedance with the substrates above and below the aligned array. Moreover, in the case of aligned structures, it is difficult to achieve high filling ratio, whereas in the case of using CNTs as filler for silicone or epoxy composites, their homogeneous dispersion in the polymer matrix would be more than a concern. Similar considerations apply for TIMs with other fillers than CNTs, where, the volume fraction and overall dimensions of the dispersed particles play a significant role in understanding how the heat will be conducted. More importantly, the ongoing research should focus on minimising the overall thermal impedance rather than improving the thermal conductivity of the composites based on theoretical models (percolation paths between particles in close contact) (Prasher 2006). Another negative aspect that contributes to uncertainties when comparing the performance of TIMs from different sources is that the materials are tested using different standard test methods. Also different implementations or modifications of the same standard may lead to discrepancies in results (Lasance et al. 2006).

3.2 Nanowire composites

In recent years there is a surge of publications in the area of metallic and semiconductor nanowire fabrication and applications as novel transistor device, sensors, biosensors, high density data storage, in energy scavenging, e.g. solar, thermoelectric, piezoelectric, etc. as well as semiconductor packaging materials to be used as z-axis interconnections, thermal interface materials, and so on. Similarly, a surge of publications was observed in the area of magnetic nanowires to explore the novel physics and material properties at reduced physical dimensions. In a recent publication, nickel nanowire and nanoparticles are used as filler materials in a nanocomposite fabrication using polydimethylsiloxane (PDMS) as polymer in order to investigate the magnetic properties of the nanocomposite (Heather et al. 2009; Sun and Keshoju 2008). For thermoelectric application, aligned Si nanowire were fabricated using vapour-liquid-solid (VLS) process and infused with low thermal conductivity and conformal polymer parylene. A thermal conductivity of 4.9±2.2 Wm⁻¹K⁻¹ was measured for the composite (Abramson et al. 2004). Similarly, bismuth telluride nanowire-epoxy composite were fabricated which showed reduced thermal conductivity and thereby a reduction in performance penalty from 27% to ~5% (Kalapi et al. 2009).

However, the use of nanowire composites as thermal interface materials seems to be limited to a few publications including ours. Recently, there are study to evaluate the complete set of effective transversely isotropic properties of a nanocomposite at various nanofiber-volume fractions through effective continuum modeling and experimental testing which used Co nanowires as filler materials. The study found significant anisotropy in the effective thermo- mechanical properties of the nanocomposite but surprisingly not in the effective Poisson's ratio and coefficient of thermal expansion (CTE) (Chen et al. 2008). Micrometer (5 and 10 μ m) long Ag and Cu nanowires having a diameter of 25 nm fabricated using template based method mixed with polystyrene. The composites attained a low percolation at a 0.25 and 0.75 vol% (Gelves et al. 2006). Further study showed that unfunctionalized Cu

nanowires having a diameter of 25 nm and length 1.78 μ m able to form electrical conductive networks at 0.5 vol% whereas for functionalized nanowires it is 0.25 vol%. The electrical resistivity of the percolated nanocomposites showed a value of 10⁶–10⁷ Ω cm (Gelves and et al. 2008). Similarly, the Ag nanowires electrical percolation behavior was studied using both simulation and experimentation by White et al. (White et al. 2010). The study of electrical and mechanical properties of nanocomposites at low volume fraction (0.1-7 vol%) of high aspect ratio structures is interesting. This is due to the ability of these nanotube/ nanowire fillers in achieving percolated network at a low volume fraction compared to spherical micron and nanoparticles.

In an attempt to increase the thermal conductivity of organic phase change materials 62.73 wt% of Ag nanowires are infused in 1-Tetradecanol. A thermal conductivity of 1.46 Wm⁻¹K⁻¹ was achieved at a high phase enthalpy of 76.5 Jg⁻¹, which was attributed to the high aspect ratio of the nanowires in the composite PCM (Zeng et al. 2009). Similarly, Ni NW/P(VDF-TrFE) composites were prepared with a volume fraction of Ni nanowires varying from 0 to 5 vol %, achieving an electrical percolation threshold at 0.75 vol%. An electrical conductivity of 10^2 Sm⁻¹ was observed for the composites using nanowires with aspect ration ~250 (Lonjon et al. 2009). Munari et al. also applied a similar approach where silver nanowires were fabricated using a polyol process and mixed with silicone elastomer (PSW 2286) using different wt% of nanowire up to a value of 7.2. A thermal impedance of 2.6 °Ccm²W⁻¹ was achieved at a pressure of 0.6 MPa with a bond line thickness of 0.5 mm. In this study, length of nanowires fabricated using polyol method has a wide variation typically ranging from 10-50 µm with an average wire diameter of 100 nm (Munari et al. 2009). In a different approach, rather than mixing the nanowires at a high wt%, we used polymer template to grow nanowires through the pores. Individual nanowires should be able to contact the heat generating and the dissipating devices and thereby with lower concentration of filler materials (Ju et al. 2009; Razeeb and Roy 2008) low impedance should be achieved. One of the interesting works which achieved low thermal impedance reported a different TIM structure, where electrospun porous polymer fiber was coated with multi-layer Ni/Au layer. This was further coated with Field's metal alloy (InBiSn) which has a melting point of ~60 °C by force infiltration to create the composite film. A thermal impedance of 8.5×10^{-2} °Ccm²W⁻¹ was reported at a pressure of 0.8 MPa with a bond line thickness of 70 µm (Carlberg et al. 2009).

4. Nanowire composites as thermal interface materials

As semiconductor device feature sizes continue to be reduced, ensuring reliable operation has become a growing challenge. The effective transfer of heat from an integrated circuit (IC) and its heat spreader to a heat sink is a vital step in meeting this challenge (Cola et al. 2008). Microscopic surface roughness and non-planarity of the IC/heat spreader and heat sink surfaces result in asperities between the two mating surfaces, which prevent the two solids from forming a thermally perfect contact due to the poor thermal conductivity of air that exists in the gaps between the two surfaces (Prasher et al. 2003). Thermal interface materials (TIM) are, therefore, used to provide an effective heat conduction path between the two solid surfaces owing to their conformation to surface roughness and high thermal conductivity (Razeeb and Roy 2008). Different TIMs such as metallic foils, grease, phase change materials, adhesives, elastomer and thermoplastic polymers have already been deployed for reducing the thermal impedance between joints (Savija et al. 2003), The thermal impedance of this system is comprised of the combined thermal contact impedances of the two surfaces and the bulk thermal impedance of the TIM material. Elastomer and thermoplastic polymer TIM composites made of a low modulus polymer matrix and high thermally conductive particle fillers are already widely used. The typical thermal impedance between joints is above 1.0 °Ccm²W⁻¹ when using traditional particle-laden elastomeric pads (Viswanath et al. 2000). However, TIMs with lower thermal impedance are required, according to the 2007 ITRS roadmap (ITRS 2007). Recently, advanced thermal management schemes using carbon nanotubes (CNTs) as filler particles in polymer or CNT arrays directly as TIMs have been suggested as a means to dissipate high heat fluxes while maintaining low chip temperatures. These proposals have been made on the basis of the high intrinsic thermal conductivity of CNTs (Prasher 2006). So far, the reported effective thermal conductivity of CNT arrays range from 74 to 83 Wm⁻¹K⁻¹, and the lowest thermal impedance between substrates obtained by using CNT array based TIMs is about 0.1 °Ccm²W⁻¹ which is an order of magnitude lower than the commercial elastomeric pad TIMs (Cola et al. 2007b). However, while using the CNT arrays as TIMs has the potential to compete with state-of-art thermal pads, the fabrication of these CNT array thermal interfaces requires high temperature (above 800 °C) processes and these are incompatible with the temperaturesensitive substrates used in most semiconductor technologies. Furthermore, the electrical performance of most metal contacts and interconnects degrades when exposed to a temperature in excess of to 450°C for more than a very limited time (Cola et al. 2007b). Using insertable CNT array as a TIM has also been reported. However, in this case the contact impedance between the CNTs and substrates was found to be high. This was associated with non-uniform growth of CNTs preventing all of the CNTs in the film from making proper thermal contact to the opposing surface. Furthermore, the high Young's modulus of CNTs (0.8~0.9 TPa for multi-wall-CNTs, 1~5 TPa for single-wall-CNTs (Srivastava et al. 2003)) prevents the array from conforming between surfaces and achieving good thermal contact (Cola et al. 2007b; Schelling et al. 2005). The possibility of inadvertently incorporating contaminating impurities, the existence of voids between CNTs, and the growth conditions of CNT arrays greatly affect the effective thermal conductivity of CNTs, typically resulting in a TIM with a large performance uncertainty. In addition, the need for mass production due to the high commercial volumes requirement and the high cost of fabrication may be another hindrance to the industrial acceptance of this solution.

In this work, we investigate a polymer composite which uses silver nanowire (AgNW) arrays - as opposed to CNT array - in a TIM. These nanowires have an average diameter of 220 nm and an aspect ratio of >100. Bulk silver has an excellent thermal conductivity of 429 Wm⁻¹K⁻¹ and it has a low Young's modulus of 83 GPa, which is far lower than that of CNTs (800 GPa). This suggests a better conformability to the rough surface of the substrates, and may permit achievement of superior thermal impedance than CNT-based TIMs. Furthermore, compared to the Ag particles/flakes which have already been widely used as fillers for many polymeric TIMs, the AgNW arrays are expected to be better effective thermal conduits due to their inherent continuity, vertically-aligned orientation and their ability to conform to micron-scale unevenness of the mating surfaces. Nanoporous polymer template can be used to fabricate these high aspect ratio nanowires by the electrodeposition techniques. However, thermal conductivity and, particularly, thermal impedance of these AgNW-polymer and CNT-polymer TIMs is necessary in order to understand the

thermal contact impedance behaviour of these two composites. As discussed above, thermal contact impedance characteristics are the performance defining parameter for any thermal interface material.

5. Fabrication and characterization of nanowire-polymer nanocomposites

5.1 Sample fabrication and material characterization

The AgNW - polymer composite was fabricated by electrodeposition using a porous polycarbonate (PC) film (Millipore, pore density: ~20%, pore diameter: ~220 nm) as a template. Typically, a 100 nm Ag thin film was deposited at the bottom of the template to act as a seed and conductive layer. A bath comprising 50 gl-1 AgNO3 and 200 gl-1 CH3COONH4 was prepared. Deionized water with resistivity $\sim 18 \text{ M}\Omega$ was used to prepare the solution. Electrodeposition was performed with stirring at a constant 500 RPM. A current density of 1 mAcm⁻² was applied and all the deposition was performed at room temperature. After deposition, the samples were thoroughly rinsed with deionized water; any Ag overgrowth was removed manually and dried with a nitrogen gun. After thermal impedance measurements of the as prepared samples, the top surface of the samples was coated with a 30 nm Au film by e-beam evaporation. This was to investigate the influence of a conductive metal layer on overall thermal impedance of the nanocomposite material. The top surface and the cross-sectional view of the AgNWs within the PC matrix were characterized by scanning electron microscopy using a JOEL 200 SEM. For an estimation of overall grain size and crystal orientation, X-ray diffraction (XRD) measurements were carried out using a Philips PW3710 diffractometer with Cu-Ka₁ radiation that had a wavelength of 1.540598 Å.

5.2 Thermal diffusivity measurements

Thermal diffusivity measurement of the AgNW-PC composites was carried out using the laser flash method (Parker et al. 1961; Razeeb and Roy 2008). A short laser pulse (using Nd:YAG laser) of duration 7 ns was applied to the samples to create an effectively instantaneous heat source. The Ag seed layer side was heated with the laser pulse where the diameter of the laser beam was 4 mm. An infrared detector was positioned on the opposite side of the sample to where the pulse impinged in order to measure the thermal response that is generated during this illumination. The resulting rise in temperature was recorded using the pre-amplifier and oscilloscope setup, which was controlled using a Labview program. In this method, heat flow is assumed to be one-dimensional in the direction perpendicular to the planar surfaces. The duration of the pulse is short enough to be considered effectively instantaneous in comparison to the time taken for the thermal response to reach half of its maximum value. The time at which the curve reaches that value is given by the following equation:

$$t_{0.5} = \frac{1.38l^2}{\pi^2 \alpha}$$
(2)

where α is thermal diffusivity, l is thickness of the sample and t_{0.5} is the time at which the thermal response at the opposite side of the sample reaches half of its maximum value. Diffusivity is calculated from the time t_{0.5} and the thickness of the samples. All the measurements were conducted in air and therefore heat loss correction for radiative and convective heat losses was done according to Cowan (Cowan 1963).

5.3 Thermal impedance measurements

To measure the thermal impedance of the composites, a modified ASTM D5470-06 standard setup was employed (Munari et al. 2009; Razeeb et al. 2007). A detailed drawing of the experimental setup can be seen in Fig. 3(a), where different components are numbered to describe the setup. The meter bars (7) are made of two round copper C11600 rods 60 mmlong and 20 mm-diameter and have a nominal thermal conductivity of 388 Wm⁻¹K⁻¹ at 25 °C. The contact surfaces were ground with a Buehler grinder apparatus and polished with 1 micron diamond paste to get a mirror finish. The surface roughness was measured with an NT-MDT model atomic force microscope (AFM). Fig 3(c) and (d) show the representative topographic and the 3D topographic images of the surface of copper calorimeter, which showed an RMS (root-mean-square) roughness of 88 nm. Eight 0.5 mm diameter thermistors were embedded within the bars to measure the thermal gradients with an accuracy of ± 0.01 °C, between 0-70 °C. Calibration of the thermistors was performed with a Hart Scientific 5611T model reference probe with an absolute calibrated uncertainty of 0.002 °C. The thermistor resistances were recorded using two National Instruments DAQ-mx USB cards, each equipped with 4-channels and each in 4-wire resistance configuration using a built-in low excitation current. Cooling of the lower meter bar was provided by a Lauda thermal bath constant-temperature cooler loop whose stability was ±0.02°C. The upper meter bar was heated using an aluminium heater block with two internal 250 W cartridge heaters controlled by a Red-Lion PID controller. The heater block was attached to an AST KAF-S Load Cell with rated load of 2 kN $\pm 0.2\%$ (11). The load cell, in turn, was then attached to Nanotec Ball Screw Linear Actuator, which can apply a maximum force of 1.8 kN onto a surface of 3.14×10-4 m². Furthermore the actuator has a minimum step size of 1 µm resolution (15). The distance between the two mating surfaces of the bars was measured using an MX-Metralight laser micrometer with a 0.4 µm resolution (10) and thereby the bond line thickness (BLT) of the sample could be measured in situ. During testing, the meter bars were wrapped in an insulating material (not shown in Fig. 3) to minimize heat losses. Calibration of the test facility was carried out by machining 4 stainless steel (303 grade) disks with different thicknesses. According to data sheets provided by the manufacturer, a nominal thermal conductivity of 15.10 Wm⁻¹K⁻¹ is expected at 29.27 °C, which is the mean temperature of the sample under test. Prior to testing, a thin layer of highly conductive thermal paste was spread onto both faces of the disk in order to minimize contact impedance as much as possible, because this differs from sample to sample depending on surface roughness. Each disk was compressed between the meter bars under a constant contact pressure of 1 MPa and the thermal impedance of the disk was measured. These measurements are plotted in Fig. 4 against their respective thicknesses. A linear fit is used for this set of data and the slope is equal to the inverse of the thermal conductivity of the bulk material. The effective thermal conductivity according to this simple calculation is found to be 15.01 Wm-1K-1 which is within 0.59% of the manufacture's value of 15.10 Wm⁻¹K⁻¹.

6. Nanowire-polymer composite as TIM

The SEM images of Fig. 5 indicate that the *as-grown* Ag arrays are vertically aligned. The top view of the nanocomposite film shows that AgNW have extruded outside the polycarbonate membrane. It should be noted that the wires were distorted while preparing the sample for cross section analysis as shown in the inset of Fig. 5(a). The nanometer-size of these AgNW tips are expected to be able to conform to the submicron roughness of the substrate surfaces. Fig. 5(b) shows the high magnification image of the top surface where the grains of the AgNW are visible.



Fig. 3. Cad design of the experimental apparatus. (a) Front view and (b) side view of the apparatus. (1) Aluminium plate (2) Fine threaded linear screw for x-y displacement. (3) Insulating Perspex plate, (4) Compression springs, (5) Aluminium shafts, (6) Aluminium cooler block, (8) Micrometer stand, (12) Perspex plate. (13) Steel plates. (14) Stainless steel Ball-Screw. (c) and (d) show the representative topographic and the 3D topographic images of the surface of copper calorimeter.



Fig. 4. Measured thermal impedance versus thickness of 303-Stainless steel disks.



Fig. 5. SEM images of AgNW arrays within PC matrix. (a) Top surface showing nanowires coming out of pores. Inset showing cross section, (b) top view (Ju et al. 2009).

The real filling ratio (ϕ) of AgNW within the PC membrane was calculated according to the following formula:

$$\varphi = \frac{V_{Ag}}{V_{T}} = \frac{(W_2 - W_1) / \rho_{Ag}}{\pi D^2 h / 4}$$
(3)

where V_{Ag} is the volume of AgNW, V_T is the total volume of the PC membrane which includes unfilled pores, W_1 is the weight before deposition and W_2 is the weight of the sample after the Ag plating process, ρ_{Ag} is the density of silver, D is the diameter of deposited area and h is the thickness of the membrane. A filling ratio of 9 vol% AgNW was obtained for the samples studied in this work.

According to the rule of mixtures for a simple parallel model, the effective thermal conductivity in the z direction is (Razeeb and Roy 2008):

$$k_z = k_m (1 - \varphi) + k_p \varphi \tag{4}$$

where k_z is the thermal conductivity of the composite material along the z direction, i.e. perpendicular to the sample surface, k_m and k_p are the bulk thermal conductivities of the matrix and the AgNW, respectively, and ϕ is the volume percentage of the AgNW in the composite. Considering that the bulk thermal conductivity of polycarbonate is 0.2 Wm⁻¹K⁻¹ and Ag is 429 Wm⁻¹K⁻¹, the calculated thermal conductivity of this composite is shown in Fig. 6, as a function of volume concentration of AgNW. The porosity of PC membrane is ~20%. Therefore, in case of 100% pore filling, the volume percentage of AgNW will be 20% in the polymer matrix. The calculated thermal conductivity value of this AgNW-PC composite is ~86 Wm⁻¹K⁻¹, which is comparable to CNT arrays (74-83 Wm⁻¹K⁻¹).

The thermal conductivity of the AgNW-PC composite was determined from the thermal diffusivity values, measured using the laser flash method described in section 5.2 and other works (Razeeb and Roy 2008). Fig. 7 shows the thermograms of silver foil (purity 99.99%, thickness 265 μ m), PC template (with a thickness of 24±1 μ m), before Ag nanowire formation (PC without AgNW) and after fabrication of AgNW-PC (thickness 24 μ m). The



Fig. 6. Thermal conductivity of AgNW-PC nanocomposite as a function of vol.% of Ag (Ju et al. 2009).

blank PC membrane with Ag seed layer on one side resulted in a thermal diffusivity of $0.0152 \times 10^{-5} \text{ m}^2\text{s}^{-1}$ and pure Ag foil (265 µm thickness) showed a diffusivity value of $17.356 \times 10^{-5} \text{ m}^2\text{s}^{-1}$. These values represent differences of 1.6% and 0.17% respectively, when compared to values of polycarbonate and silver in the literature (Weast 1994). The values obtained for the composite varied from 1.82×10^{-5} to $1.96 \times 10^{-5} \text{ m}^2\text{s}^{-1}$ and showed an average value of $1.89 \times 10^{-5} \text{ m}^2\text{s}^{-1}$. This shows a significant increase in the diffusivity of the composite to that of blank PC a factor of 124.



Fig. 7. Thermal transients of AgNW-PC, PC template without AgNW and silver foil (Ju et al. 2009).

Combining with the experimental thermal diffusivity value, the Eq. (4) can be written as,

$$k_{NC} = k_{PC}(1-\phi) + k_{Ag}\phi = \alpha[(\rho c)_{PC}(1-\phi) + (\rho c)_{Ag}\phi]$$
(5)

where k is the thermal conductivity and (ρc) is heat capacity per unit volume. φ is the volume percentage of Ag in the composite and α is the thermal diffusivity of the composite. For 9% filling ratio of AgNW (as achieved in this paper), the calculated thermal conductivity is ~38.8 Wm⁻¹K⁻¹ according to equation 4. However, a thermal conductivity of 30.3 Wm⁻¹K⁻¹ was evaluated (using Eq. 5) for the nanocomposite using the experimental diffusivity value and considering the density and the heat capacity of silver and polycarbonate. It is interesting to note that the calculated thermal conductivity value of the nanocomposite (k_{NC}) (38.8 Wm⁻¹K⁻¹) using the modified effective medium theory, over-predicted the experimental values when the bulk thermal conductivity of Ag was considered. However, when the thermal conductivity of Ag was reduced to ~78% of the bulk conductivity, the theoretical value showed excellent correspondence. In this case, AgNW have an effective thermal conductivity of 334.6 Wm⁻¹K⁻¹. In order to understand this conductivity reduction, an XRD analysis was carried out on AgNW samples. The XRD analysis revealed that the AgNW are polycrystalline with a preferred orientation of (111). The Scherrer formula was employed to calculate the grain size of the AgNW, which showed an average grain size of 204 nm. A similar reduction in conductivity value for Ni nanowires has already been observed as an effect of grain size (Razeeb and Roy 2008). The deviation from bulk thermal conductivity in case of AgNW may be explained as follows: The thermal conduction in pure metals is usually dominated by electron rather than phonon conduction. Therefore, the thermal conductivity and diffusivity are dominated by the scattering process of conducting electrons. At room temperature, the electron mean free path of Ag is 52 nm (Zhang et al. 2004). Although the average grain size obtained from XRD measurements is 4 times the mean free path of the electron, it was reported that the grain size of electrodeposited silver NW could vary from ~10 to ~200 nm (Kazeminezhad et al. 2007). In electrodeposited AgNW, there are also large numbers of defects and dislocations in crystals and, therefore, the grain boundary scattering of conduction electrons is believed to be responsible for the reduction in measured thermal conductivity over the expected theoretical value.

In a publication by Huang et al. (Huang et al. 2009) it was shown that the electrical resistivity of a single crystalline trapezoidal silver Ag nanowire is dominated by the electron diffusely scattering on the nanowire surface and explained their experimental results using Chamber's approach (Chambers 1950) to the FS (Fuchs and Sondheimer) theory (Fuchs 1938; Sondheimer 1952). Their work was focused to differentiate the surface scattering from the grain boundary scattering and for single crystal wires the experimental resistivity fit well to the theoretical resistivity models that are close to purely diffuse surface scattering. Durkan et al. (Durkan and Welland 2000) on the other hand, argued that in a polycrystalline wire, when the wire width is comparable to the average grain size, the grain boundary scattering is the dominant source of increased resistivity. Only when the wire width is below ~ 0.5 times the grain size, surface scattering becomes important and approaches to the same order of magnitude of grain boundary scattering. Similarly, it was observed that the surface scattering is intimately connected with the geometrical dimensions, i.e. diameter of the wires. This scatting becomes important when the diameter is comparable to or smaller than the mean free path of the conduction electrons of the respective metal (Steinhögl et al. 2002). In the present case, the nanowires are polycrystalline with an average grain size is \sim 204 nm and have a diameter of 220 nm, which is comparable to the grain size. Thereby, the grain boundary scattering will be the dominant factor in reducing the thermal diffusivity and conductivity of the Ag nanowires, rather than surface scattering.

The thermal impedances of the as-prepared AgNW-PC composite films with (AgNW-PCtop metal layer) and without the top metal layer (AgNW-PC) are shown in Fig. 8 as a function of applied contact pressure. To facilitate comparison, a blank PC template, with a 100 nm Ag seed layer and a commercially-available thermal pad are also included. The thermal impedance of the PC membrane before and after seed layer deposition did not show a large variation, specifically when the contact pressure exceeded 0.2 MPa. In the lower contact pressure range, the seed layer acted as a heat spreader and enhanced the heat transfer, which resulted in a further reduction of measured thermal impedance. However, as the contact pressure was increased, this effect diminished. The thermal impedance of the AgNW-PC composite sample showed at least a 61% reduction compared to the PC with seed layer under all measured contact pressures and a 29% reduction compared to commercial thermal pad. When a 30 nm Au film was deposited on top of the AgNW-PC film, the thermal impedance was reduced by another 35%, to 0.93 °Ccm²W⁻¹ at a contact pressure of 1.0 MPa. The SEM analysis on different areas of the AgNW-PC samples revealed that not all of the nanowires came out of the pores due to non-homogeneity in the pore structure. The deposited Au film effectively connected most of the nanowires together and thereby increased the effective contact area. As a result, the thermal impedance decreased, which was also reported for carbon nanotube arrays (Panzer et al. 2008; Wu et al. 2005). This limiting of contact area (without top metal layer) leads to an increase in the contact impedance, ultimately increasing the overall impedance of the TIM. The contribution of contact impedance will be explored in section 7.



Fig. 8. Thermal impedance (with error bars) of AgNW-PC composite and reference samples as a function of contact pressure (Ju et al. 2009).

7. Contact impedance model

The two most important parameters for a thermal interface material is its thermal contact impedance and bulk conductivity. The following section employs a thermal impedance model (Singhal et al. 2004) to explore how these two parameters affect the thermal impedance as a function of decreasing bond line thickness for both aligned AgNW and aligned CNT embedded in a polycarbonate matrix. With decreasing bond line thickness, the percentage contribution of the contact to overall thermal impedance increases and is of critical importance to the thermal behaviour of an interface material. According to Singhal et al. (Singhal et al. 2004), the thermal contact impedance of two mating surface can be calculated from Eq. 6:

$$R_{c} = \frac{1}{1.55} \left(\frac{\sigma}{\tan\theta}\right) \left[\frac{E_{NC} \tan\theta}{\sqrt{2p}(1 - v_{e}^{2})}\right]^{0.94} \frac{1}{2} \left(\frac{1}{k_{1}} + \frac{1}{k_{NC}}\right)$$
(6)

where p is the contact pressure, σ is the RMS surface roughness, tan θ is the average slope of the asperities of the two contact surfaces and is equal to $0.125\sigma^{0.402}$, k_1 and k_{NC} are the thermal conductivity of the mating surface and composite respectively, v_e is the Poisson's ratio and E_{NC} the Young's modulus of the composite. In this case, the mating surfaces are the composite's surface and the surface of a copper calorimeter (used in the thermal impedance measurement) with a RMS roughness of 88 nm.

A modified effective medium theory (Eq. 4) is used to calculate the equivalent elastic modulus and effective Poisson's ratio of both the composites. The thermal conductivity of the CNT-polycarbonate composite is calculated by Eq. 7, developed by Nan et al. (Nan et al. 2003):

$$k_{e} = \left(1 + \frac{fk_{c}}{3k_{m}}\right)k_{m}$$
⁽⁷⁾

where k_e is the effective conductivity of the composite, k_c and k_m the thermal conductivity of the CNT and matrix respectively and f the fractional volume content of the CNTs. The effective thermal conductivity of the AgNW-PC is taken as 30.3 Wm⁻¹K⁻¹ from the thermal diffusivity measurements. It should be noted that for these calculations an intrinsic thermal conductivity of 6000 Wm⁻¹K⁻¹ is used for the CNTs. However it is has been shown that aligned CNT material has generally a far lower thermal conductivity value (Gogotsi 2006), typically 3000 Wm⁻¹K⁻¹. The parameters and the associated values used in the contact impedance model are shown in Table 2.

Materials	Young's Modulus (Pa)	Poisson's Ratio	Thermal conductivity (Wm ⁻¹ k ⁻¹)
Copper calorimeter	117×109	0.37	388
Silver	83×109	0.37	429
Polycarbonate	2.3×10 ⁹	0.37	0.2
CNT	80×10^{10}	0.08	6000
Silver-polycarbonate composite	6.3×10 ⁹	0.37	38.8 9% vol. of AgNW
CNT-polycarbonate composite	4.5×10 ¹⁰	0.35	180 9% vol. of CNT

Table 2. Values used in contact impedance calculations (Ju et al. 2009; Weast 1994).

As can be seen from Fig. 9(a), AgNW-PC has a significantly lower contact impedance than that of the aligned CNT-PC, for all contact pressure ranges up to 1 MPa. Although there is an increase in the thermal conductivity of the polycarbonate matrix by the introduction of the CNT's, the increase in the contact impedance due to the stiffening of the composite essentially diminishes much of the gain. Since the Young's modulus of the silver used in the polycarbonate is an order of magnitude lower than that of CNTs, AgNW-PC composite does not suffer from this problem to the same extent. It was also observed that if the bond line thickness of the material is increased; the contact impedance becomes less of a concern in the overall (total) thermal impedance of the composite. This is shown in Fig. 9(b) (at a set contact pressure of 0.5 MPa) and, as would be expected, the CNT-polycarbonate composite surpasses the AgNW composite at the larger bond line thickness, in this case at 0.95 mm. This essentially showing that for thinner TIM, the most important aspect is the Young's modulus and not the intrinsic thermal conductivity.



Fig. 9. (a) Contact impedance produced by 9% volume loaded AgNW aligned in a polycarbonate matrix (9% AgNW-PC) and aligned 9% volume loaded CNT in a polycarbonate matrix (9% CNT-PC) as a function of contact pressure, with a fixed bond line thickness of 30 μ m. (b)Thermal impedance produces by 9% volume loaded AgNW aligned in a polycarbonate matrix (9% AgNW-PC) and aligned 9% volume loaded CNT in a polycarbonate matrix (9% CNT-PC) as a function of bond line thickness at a fixed contact pressure of 0.5 MPa (Ju et al. 2009).

8. Conclusion

Silver nanowire arrays embedded inside polycarbonate templates are investigated as a viable thermal interface material (TIM) for electronic cooling applications. The composite shows an average thermal diffusivity value of $1.89 \times 10^{-5} \text{ m}^2\text{s}^{-1}$, which resulted in an intrinsic thermal conductivity of 30.3 Wm⁻¹K⁻¹. The protrusion of nanowires from the polymer film surface enables it to conform to surface roughness and this result in a reduction in thermal impedance of 61%, when compared to a blank template. A thin Au film on the top of the composite was found to act as a heat spreader, which further reduced the thermal impedance value by 35%. With emphasis on the contact impedance influence on the overall thermal impedance, it is shown through the contact impedance model that, for any thermal interface material, when there is decrease in the thickness; the Young's modulus becomes the dominant factor as opposed to its intrinsic thermal conductivity.

9. References

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Poly(butylene terephthalate) Nanocomposites Containing Carbon Nanotube

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1. Introduction

Carbon nanotube (CNT) has attracted of great interest as advanced nanoreinforcements in new kinds of polymer nanocomposites because of the combination of its unique extraordinary properties with high aspect ratio and small size (Ebbesen, 1997; Dresselhaus et al., 2001; Schadler et al., 1998; Ajavan, 1999; Bokobza, 2007; Paul & Robesson, 2008). In particular, excellent mechanical strength, thermal conductivity, and electrical properties of CNT have created a high level of activity in materials research and development for potential applications such as fuel cell, hydrogen storage, field emission display, chemical or biological sensor, and advanced polymer nanocomposites (Iijima, 1991; De Heer et al., 1995; Wong et al, 1997; Fan et al., 1999; Kim & Lieber, 1999; Liu et al., 1999; Kong et al., 2000; Ishihara et al., 2001; Alan et al., 2003; Wu & Shaw, 2005). This feature has motivated a number of attempts to fabricate CNT/polymer nanocomposites in the development of highperformance composite materials (Kim et al., 2006; Kim et al., 2007; Kim et al., 2008; Kim, 2009; Kim et al., 2009; Kim et al., 2010). In this regard, much research and development have been performed to date for achieving the practical realization of excellent properties of CNT for advanced polymer nanocomposites in a broad range of industrial applications. However, because of high cost and limited availability, only a few practical applications in industrial fields such as electronic and electric appliances have been realized to date.

The CNT consisting of concentric cylinder of graphite layers is a new form of carbon and can be classified into three types (Dresselhaus et al., 2001; Iijima, 1991; Shonaike & Advani, 2003): single-walled CNT (SWCNT), double-walled CNT (DWCNT), and multi-walled CNT (MWCNT). SWCNT consists of a single layer of carbon atoms through the thickness of the cylindrical wall with the diameters of 1.0-1.4 nm, two such concentric cylinders forms DWCNT, and MWCNT consists of several layers of coaxial carbon tubes, the diameters of which range from 10 to 50 nm with the length of more than 10 µm (Dresselhaus et al., 2001; Iijima, 1991; Shonaike & Advani, 2003). The graphite nature of the nanotube lattice results in a fiber with high strength, stiffness, and conductivity, and higher aspect ratio represented by very small diameter and long length makes it possible for CNTs to be ideal nanoreinforcing fillers in advanced polymer nanocomposites (Thostenson et al., 2001). Both theoretical and experimental approaches suggest the exceptional mechanical properties of CNTs ~100 times higher than the strongest steel at a fraction of the weight (Goze et al., 1999; Yao et al., 2001;

Yu et al., 2000a; Yu et al., 2000b): The Young's modulus, strength, and toughness of SWCNT shows 0.32~1.47 TPa of Young's modulus, 10-52 GPa of strength, and ~770 J/g of toughness, respectively (Yu et al., 2000a). For MWCNT, the values of strength, Young's modulus, and toughness were found to be 11-63 GPa, 0.27-0.95 TPa, and ~1240 J/g, respectively (Yu et al., 2000b). In addition, CNTs exhibit excellent electrical properties and electric current carrying capacity ~1000 times higher than copper wires (Frank et al., 1998). In general, MWCNTs show inferior mechanical performance as compared to SWCNTs. However, MWCNTs have a cost advantage, in that they can be produced in much larger quantities at lower cost compared with the SWNT. In addition, MWCNTs are usually individual, longer, and more rigid than SWCNTs. Because of their remarkable physical properties such as high aspect ratio and excellent mechanical strength, MWCNTs are regarded as prospective reinforcing fillers in high performance polymer nanocomposites. For these reasons, extensive research and development have been directed towards the potential applications of CNTs for novel composite materials in a wide range of industrial fields. The fundamental research progressed to date on applications of CNTs also suggests that CNTs can be utilized as promising reinforcements in new kinds of polymer nanocomposites with remarkable physical/chemical characteristics (Shonaike & Advani, 2003).

Poly(butylene terephthalate) (PBT) is a semi-crystalline polymer with good mechanical properties and excellent processability, and it has been widely used as structural materials in the automotive, electrical, and electronic industries (Fakirov, 1993; Rubin, 1990; Tjong & Meng, 1999). Recently, there are continuing practical demands for realizing higher performance of PBT with various processing conditions, thus making it possible to be utilized in various advanced industries. For this reason, much research has been performed to date to extend and develop commercial applications of PBT for high performance polymer nanocomposite using reinforcing fillers as well as to displace PBT (Kim et al., 2005; Kim et al., 2006c; Wu et al., 2007; Kim, 2009b). Although promising, however, insufficient mechanical properties and thermal stability of PBT composites have often hindered its potential application in a broad range of industrial fields. From both an economic and industrial perspective, the major challenges for high performance polymer nanocomposites with low costs and to facilitate large scale-up for commercial applications.

During the rapid advancement in the materials science and technology, much research has extensively undertaken on high-performance polymer composites for targeted applications in numerous industrial fields. Furthermore, a great number of efforts have been made to develop high-performance polymer nanocomposites with the benefit of nanotechnology (Ajayan, 1999; Bokobza, 2007; Paul & Robesson, 2008). These attempts include studies of the polymer composites with the introduction of nanoreinforcing fillers into the polymer matrix (Ajayan, 1999; Bokobza, 2007; Paul & Robesson, 2008; Kim et al., 2006; Kim et al., 2007; Kim et al., 2008; Kim, 2009; Kim et al., 2010). Polymer nanocomposites, which is a new class of polymeric materials based on the reinforcement of polymers using nanofillers, have attracted a great deal of interest in fields ranging from basic science to the industrial applications because it is possible to remarkably improve the physical properties of composite materials at lower filler loading (Paul & Robesson, 2008). Therefore, the fabrication of the polymer nanocomposites reinforced with various nanofillers is believed to a key technology on advanced composites for next generation.

Currently, four processing techniques are in common use to incorporate CNT into the polymer matrix for fabricating CNT/polymer nanocomposites (Kim et al., 2006; Kim et al., 2007; Kim et al., 2008; Kim, 2009; Kim et al., 2009; Kim et al., 2010; Haggenmuller et al., 2000; Pötschke et al.,

2002; Jung et al., 2008; Mu et al., 2008; Pegel et al., 2008; Moniruzzaman & Winey, 2006): direct mixing, solution method, in situ polymerization, and melt blending. Of these processing techniques, a melt blending has been accepted as the simplest and the most effective method, particularly from a commercial perspective, because this process makes it possible to fabricate high-performance polymer nanocomposites at low process cost and facilitates commercial scale-up (Kim et al., 2006; Kim et al., 2007; Kim et al., 2008; Kim, 2009; Kim et al., 2009; Kim et al., 2010). Furthermore, the combination of a very small quantity of expensive CNT with conventional cheap thermoplastic polymers provides attractive possibility for enhancing the physical properties of polymer nanocomposites using a simple and cost-effective method. This chapter focuses on the fabrication and characterization of CNT-reinforced PBT nanocomposites. The PBT nanocomposites were characterized by means of advanced rheometric expansion system (ARES) rheometer, dynamic mechanical thermal analysis (DMTA), transmission electron microscopy (TEM), scanning electron microscopy (SEM), differential scanning calorimetry (DSC), and thermogravimetric analysis (TGA) to clarify the effects of CNT on the physical properties of PBT nanocomposites. It is expected that this chapter will help in the preliminary understanding of the fabrication and enhanced properties of PBT nanocomposites reinforced with a very small quantity of CNT. This chapter also suggests a simple and cost-effective method that will facilitate the industrial realization of CNT-reinforced PBT nanocomposites with enhanced physical properties.

2. Fabrication of PBT nanocomposites containing CNT

2.1 General features

PBT nanocomposites containing CNT were prepared by simple melt blending in a twinscrew extruder to create high performance polymer nanocomposites at low manufacturing cost for practically possible application in a broad range of industry. There is significant dependence of thermal, rheological, and mechanical properties of PBT nanocomposites on the content and dispersion state of CNT. Storage modulus and loss modulus of PBT nanocomposites increased with increasing frequency, and this enhancing effect was more pronounced at low-frequency region. Non-terminal behavior of PBT nanocomposites was attributed to nanotube-nanotube or polymer-nanotube interactions, and the dominant nanotube-nanotube interactions at high CNT content resulted in the formation of the interconnected or network-like structures of CNT in PBT nanocomposites. A very small quantity of CNT substantially improves the mechanical properties and heat distortion temperature of PBT nanocomposites. Unique character of CNT dispersed in PBT matrix resulted in the physical barrier effect against the thermal decomposition, leading to the enhanced thermal stability of PBT nanocomposites. The key to improve the overall properties of PBT nanocomposites depend on the optimization of the unique geometry and dispersion state of CNT in PBT nanocomposites during melt processing. This chapter also suggests a simple and cost-effective method that will facilitate the industrial realization of CNT-reinforced PBT nanocomposites with enhanced physical properties.

2.2 CNT-reinforced PBT nanocomposites

PBT was used as the thermoplastic polymer with an intrinsic viscosity of 1.1 dl/g and a melt-flow index of 20 g/min, supplied by Samyang Corp., Korea. The nanotubes used were multiwalled CNT (degree of purity > 95%) synthesized by a thermal chemical vapor deposition process, purchased from Iljin Nanotech, Korea. According to the supplier, their

length and diameter were 10–30 nm and 10–50 µm, respectively, indicating that their aspect ratio reaches 1000. All materials were dried at 120°C *in vacuo* for at least 24 h before use to minimize the effects of moisture. PBT nanocomposites were prepared by a melt blending process in a Haake Rheometer (Haake Technik GmbH, Germany) equipped with the intermeshing co-rotating type of a twin-screw. The temperatures of the heating zone, from the hopper to the die, were set to 250, 260, 265, and 255°C, and the screw speed was fixed at 45 rpm. Prior to melt blending, PBT and CNT were physically premixed before being fed in the hopper of a twin-screw extruder to achieve better dispersion of CNT with PBT. For the fabrication of PBT nanocomposites, PBT was melt-blended with the addition of CNT content, specified as 0.5, 1.0, and 2.0 wt % in the polymer matrix. Upon completion of melt blending, the extruded strands were cooled in the water-bath and then cut into pellets using a rate-controlled pelletizer.

3. Effect of CNT on properties of PBT nanocomposites

3.1 Rheological properties

The complex viscosity $(|\eta^*|)$ of PBT nanocomposites as a function of frequency is shown in Figure 1. The $|\eta^*|$ values of PBT nanocomposites decreased with increasing frequency, indicating a non-Newtonian behavior over the whole frequency range measured. The shear thinning behavior of PBT nanocomposites was attributed to random orientation and entangled molecular chains in the polymer nanocomposites during the applied shear force. The effect of CNT on the $|\eta^*|$ value of PBT nanocomposites was more significant at lowfrequency region than at high-frequency region, and this effect decreased with increasing frequency because of strong shear thinning behavior of PBT nanocomposites induced by CNT. As shown in Figure 1B, PBT nanocomposites exhibited higher $|\eta^*|$, particularly at low frequency as compared to pure PBT, indicating the formation of interconnected or networklike structures as a result of particle-particle and particle-polymer interactions (Kim, 2009b; Kim et al., 2008; Kim et al., 2006). The PBT nanocomposites exhibited shear thinning behavior, resulting from the breakdown of these structures with increasing frequency. For understanding the effect of CNT on the rheological behavior of PBT nanocomposites, it is also very instructive to characterize the variations of the shear thing exponent for PBT nanocomposites (Abdel-Goad & Pötscke, 2005). In the case of an ideal Newtonian fluid, the shear thinning exponent approaches or equals 0 and the viscosity is independent of the frequency, thus exhibiting the terminal flow behavior, whereas for the polymer nanocomposites, as the shearing thinning behavior develops, the shearing thinning exponent increases with increasing filler concentration (Abdel-Goad & Pötscke, 2005; Costa et al., 2006; Krishnamoorti & Giannelis, 1996; Krishnamoorti & Giannelis, 1997). The shear thinning exponent can be obtained from the slope of the plot of $|\eta^*|$ versus ω for PBT nanocomposites. As shown in Table 1, the shear thinning exponent of PBT nanocomposites slightly decreased with the introduction of CNT, and this effect was more pronounced at high CNT content, indicating significant dependence of the shear thinning behavior of PBT nanocomposite on CNT content.

The storage modulus (G') and loss modulus (G'') of PBT nanocomposites as a function of frequency are shown in Figure 2. The values of G' and G'' for PBT nanocomposites increased with increasing frequency, and this enhancing effect was more pronounced at low-frequency region. This rheological response is similar to the relaxation behavior of the typical filled-polymer composite systems (40-43). If polymer chains are fully relaxed and



Fig. 1. (A) Complex viscosity ($|\eta^*|$) of PBT nanocomposites as a function of frequency. (B) Variations of $|\eta^*|$ of PBT nanocomposites with the CNT content at different frequencies. Reproduced with permission from Ref. (Kim, 2009b). © 2009 Wiley Periodicals, Inc.

Materials	Slope of $ \eta^* $ versus ω	Slope of G' versus ω	Slope of G'' versus ω
PBT	-0.1389	0.7639	0.7342
PBT/CNT 0.5	-0.1548	0.4286	0.5081
PBT/CNT 1.0	-0.3643	0.4030	0.5043
PBT/CNT 2.0	-0.7592	0.3128	0.4255

Table 1. Low-frequency slopes of $|\eta^*|$, *G*', and *G*'' versus ω for PBT nanocomposites

exhibit a characteristic homopolymer-like terminal behavior, the flow curves of polymers can be expressed by a power law of $G' \propto \omega^2$ and $G'' \propto \omega$ (Ferry, 1980). Krishnamoorti and Giannelis reported that the slopes of G' and G" for the polymer/layered silicate nanocomposites were much smaller than 2 and 1, respectively, suggesting that large deviations in the presence of a small quantity of layered silicate were caused by the formation of network-like structures in the molten state (Krishnamoorti & Giannelis, 1997). The variations of the slopes of the terminal zone of G' and G'' for PBT nanocomposites indicate the non-terminal behavior with the powerlaw dependence for G' and G'' of PBT nanocomposites (Table 1). Similar observations have been reported in the ordered block copolymers and the smectic liquid-crystalline small molecules (Rosedalev & Bates, 1990; Larson et al., 1993). The decrease in the slopes of G' and G'' for PBT nanocomposites with increasing CNT content was explained by the fact that the nanotube-nanotube or the polymer-nanotube interactions (Kim, 2009b; Kim et al., 2008; Kim et al., 2006) can lead to the formation of the interconnected or network-like structures, resulting in the pseudo solid-like behavior of PBT nanocomposites. As shown in Figure 2, the extent of the increase in G' of PBT nanocomposites was higher than that of G'' over the whole frequency range measured, and the values of G' and G" of PBT nanocomposites were higher than those of pure PBT, particularly at low frequency. This result demonstrates that the interconnected or network-like structures can be formed in PBT nanocomposites via the nanotube-nanotube or polymer-nanotube interactions in the presence of CNT, resulting in more elasticity of PBT nanocomposites. As the applied frequency increased, the interconnected or network-like structures were broken down due to high levels of shearing force, and PBT nanocomposites exhibited almost similar or slight higher G' and G'' values than those of pure PBT at high frequency.



Fig. 2. (A) Storage modulus (G') and (B) loss modulus (G'') of PBT nanocomposites as a function of frequency. Reproduced with permission from Ref. (Kim, 2009b). © 2009 Wiley Periodicals, Inc.

The variations of tan δ as a function of frequency for the PBT nanocomposites are shown in Figure 3A. Shear deformation can lead to partial orientation of the molecules in polymer chains, and tan δ decreased with increasing frequency. The maximum of tan δ for PBT nanocomposites shifted toward high-frequency region with increasing CNT content, indicating the formation of densely interconnected or network-like structures in PBT nanocomposites (Kim, 2009b; Kim et al., 2008; Kim et al., 2006). Figure 3B shows the plots of the phase angle (δ) versus the absolute values of the complex modulus ($|G^*|$) for the PBT nanocomposites, which is known as the Van Gulp-Palmen plot (Van Gulip & Palmen, 1998). It can be seen that a significant change in the δ values occurred with the introduction of CNT. For PBT nanocomposites, the decrease in the δ values with decreasing the $|G^*|$ values indicated that the incorporation of CNT into PBT matrix enhanced the elastic behavior of PBT nanocomposites. The plots of log G' versus log G" for PBT nanocomposites are shown in Figure 4. In general, this plot provides a master curve with a slope of 2 for isotropic and homogeneous polymer melts, irrespective of temperature (Han et al., 1989). However, PBT nanocomposites did not provide a perfect single master curve and exhibited the shifting and change of the slope with the introduction of CNT. The slopes in the terminal regime of PBT nanocomposites were less than 2, indicating that PBT nanocomposite systems were heterogeneous and they underwent some chain conformational changes because of the interconnected or network-like structures via the nanotube-nanotube or nanotube-polymer interactions in the presence of CNT (Kim, 2009c; Kim et al., 2008; Kim et al., 2006). However, over the higher G" values, the slopes of PBT nanocomposites increased and approached similar slope of pure PBT, indicating that the interconnected or network-like structures formed in PBT nanocomposites were broken down by high levels of shear force.

3.2 Dynamic mechanical properties

The dynamic mechanical properties of PBT nanocomposites are shown in Figure 5. There is a significant dependence of the storage modulus (*E*') and the tan δ for PBT nanocomposites on the temperature and the presence of CNT. As the molecular motions within the polymer nanocomposites change, the storage modulus of the polymer nanocomposites varied with the temperature. The *E*' values of PBT nanocomposites decreased rapidly, whereas the tan δ underwent a maximum when the polymer nanocomposites were heated through the glass



Fig. 3. (A) Variations of tan δ of PBT nanocomposites as a function of frequency. (B) Plots of the phase angle (δ) versus the complex modulus ($|G^*|$) of PBT nanocomposites. Reproduced with permission from Ref. (Kim, 2009b). © 2009 Wiley Periodicals, Inc.



Fig. 4. Plots of log *G*′ versus log *G*″ for PBT nanocomposites. Reproduced with permission from Ref. (Kim, 2009b). © 2009 Wiley Periodicals, Inc.

transition region. The incorporation of CNT into PBT matrix significantly increased the E' values of PBT nanocomposites, which was attributed to the physical interactions between PBT and CNT with high aspect ratio and large surface areas as well as the stiffening effect of CNT as nanoreinforcing fillers, making it possible for them to allow efficient load transfer in PBT nanocomposites. As shown in Figure 5, the tan δ peaks of PBT nanocomposites as a function of temperature were not significantly affected in the presence of CNT, whereas the peak height was decreased with the introduction of CNT.

3.3 Morphology

SEM and TEM microphotographs of CNT and PBT nanocomposites are shown in Figure 6. The CNT exhibited highly curved and randomly coiled features and typically tends to bundle together or some agglomerated organization because of the intrinsic van der Waals attractions between the individual nanotubes in combination with high aspect ratio and large surface area



Fig. 5. Dynamic mechanical properties of PBT nanocomposites as a function of temperature. Filled and open circles represent the values of E' and tan δ for pure PBT and PBT/CNT 2.0 nanocomposites. Reproduced with permission from Ref. (Kim, 2009b). © 2009 Wiley Periodicals, Inc.



Fig. 6. SEM micrograph of (A) CNT and (B) PBT/CNT 2.0 nanocomposites. TEM images of PBT nanocomposites containing (B) 0.5 wt% and (C) 2.0 wt% of CNT. Reproduced with permission from Ref. (Kim, 2009b). © 2009 Wiley Periodicals, Inc.

(Ebbesen, 1997; Dresselhaus et al., 2001). As shown in Figure 6A, CNTs were randomly oriented and formed the interconnected or network-like structures in PBT nanocomposites. The CNT with a small size, high aspect ratio, and large surface area are often subjected to self-agglomeration or bundle formation at higher concentration of CNT and thus easily form interconnected or network-like structures in the molten polymer matrix (Schadler et al, 1998). Some CNT bundles were pulled out from PBT matrix and some of them were individually dispersed in the polymer matrix. As shown in Figure 6C, TEM image of PBT nanocomposites containing 0.5 wt% of CNT showed that the dispersion of CNT was quite good. However, at high CNT content, less uniformly dispersed and highly entangled CNT structures were observed in PBT nanocomposites. The CNT was, on a large scale, uniformly dispersed in the polymer matrix despite some agglomerated CNT structures, and PBT nanocomposites exhibited relatively more uniform dispersion of CNT in PBT matrix particularly at lower CNT content in comparison with them at higher CNT content.

3.4 Mechanical properties

The mechanical properties of PBT nanocomposites with the CNT content are shown in Figure 7. There is a significant dependence of the mechanical properties of PBT nanocomposites on the CNT content. The incorporation of a very small quantity of CNT into PBT can substantially improve the mechanical properties of PBT nanocomposites due to the nanoreinforcing effect of CNT with high aspect ratio and uniform dispersion in the polymer matrix. The PBT nanocomposites exhibited higher tensile strength and tensile modulus than those of pure PBT. For instance, on the incorporation of CNT, the tensile strength and tensile modulus of PBT nanocomposites were significantly increased by 35.1 and 21.7%, respectively, and this enhancing effect was more significant at low CNT content as compared to high CNT content. The fact that the improvement in the mechanical properties of PBT nanocomposites was not increased at higher CNT content as expected, in comparison with that at low CNT content, can be explained by the characteristics of CNT that tended to bundle together because of their intrinsic van der Waals attractions between the individual nanotubes in combination with high aspect ratio and large surface area and could lead to some agglomeration, causing the stress concentration phenomenon and preventing efficient load transfer to the polymer matrix (Ajayan, 1999; Bokobza, 2007; Paul & Robesson, 2008). Similar observation has been reported that for CNT/polypropylene (PP) nanocomposite systems, adding a low level of CNT into PP improved the mechanical properties of CNT/PP nanocomposites, while at high CNT content, their mechanical properties decreased via stress concentration by the nanotube aggregation (Gorga & Cohen, 2004). The poor adhesion between CNT and PP as well as imperfection and defects in the nanotube structures resulted in the reduced mechanical properties of CNT/PP nanocomposites. For achieving further enhanced mechanical properties of PBT nanocomposites, the improvement in the dispersion state of CNT and the interfacial adhesion between two phases should be required (Kim et al., 2008). The elongation at break of PBT nanocomposites decreased with the introduction of CNT, indicating that PBT nanocomposites became somewhat brittle as compared to pure PBT due to the increased stiffness of PBT nanocomposites and the micro-void formed around the nanotubes during tensile testing. As shown in Figure 7B, the flexural strength and flexural modulus of PBT nanocomposites also increased with the introduction of CNT. This enhancement of the flexural strength/modulus was attributed to the reinforcement of PBT by incorporating the dispersed CNT and the moderate transfer of the applied stress between PBT and CNT. In addition, the enhancement of the flexural modulus of PBT nanocomposites was closely related to the improvement in the value of heat distortion temperature, which will be elaborated in the following section.



Fig. 7. Variations of (A) tensile strength and tensile modulus and (B) flexural strength and flexural modulus of PBT nanocomposites with the CNT content. Reproduced with permission from Ref. (Kim, 2009b). © 2009 Wiley Periodicals, Inc.

For characterizing the effect of CNT on the mechanical properties of PBT nanocomposites, it is also very instructive to compare the reinforcing efficiency of CNT for a given content in PBT nanocomposites. The variations of the reinforcing efficiency of CNT in PBT nanocomposites are shown in Figure 8. The reinforcing efficiency of CNT can be defined as the normalized mechanical properties of PBT nanocomposites with respect to those of pure PBT as follows:

Reinforcing efficiency (%) =
$$\frac{M_c - M_m}{M_m} \times 100$$
 (1)

where M_c and M_m represent the mechanical properties, including tensile strength, tensile modulus, flexural strength, and flexural modulus, of PBT nanocomposites and pure PBT, respectively. The enhancing effect of the mechanical properties by incorporating CNT was more significant at low CNT content than at high content, indicating that a low CNT loading was more effective in improving the overall mechanical properties of PBT nanocomposites. At higher CNT content, CNT tends to bundle together and to form some agglomeration because of intrinsic van der Waals attractions between the individual nanotubes and lead to the stress concentration phenomenon, thus preventing the efficient load transfer to the polymer matrix. This result demonstrates that the incorporation of relatively small quantity of CNT into PBT matrix is more effective in the enhancement of the overall mechanical properties of PBT nanocomposites induced by high nanoreinforcing efficiency of CNT as well as good dispersion of CNT in the polymer matrix at lower concentration.

3.5 Heat distortion temperature

The elevated temperature property, typically estimated by heat distortion temperature (HDT), plays a critical role in determining the performance of engineering plastics. The HDT value is in common use to represent the upper limit of the dimensional stability of polymers in service without significant physical deformations under a normal load and thermal effect, providing important information for product design (Petaro, 2000; Wong, 2003). The HDT values can be influenced by various factors such as the melt and mold temperatures, the nucleating agent, and various processing conditions, which can be related to the mechanical behavior of polymer composites. As shown in Figure 9, the HDT values of PBT nanocomposites increased



Fig. 8. Reinforcing efficiency of CNT on the mechanical properties of PBT nanocomposites. Reproduced with permission from Ref. (Kim, 2009b). © 2009 Wiley Periodicals, Inc.

with increasing CNT content, which can be explained by the improvement in the modulus of the PBT nanocomposites. According to Nielsen's prediction (Nielsen, 1974), the variation of the HDT value was closely related to the behavior of flexural modulus with the filler content. The increase in the HDT values of PBT composites with increasing CNT content was in good agreement with the results of the flexural modulus of PBT nanocomposites as shown in Figure 7B, conforming to the Nielsen's prediction. The increased HDT values of PBT composites were attributed to the improvement in the flexural modulus with increasing CNT content. In the HDT measurements, the ability of polymeric materials to retain stiffness with increasing temperature is important for high HDT values (Thomasson & Groenewoud, 1996). As shown in Figure 5, the introduction of CNT could make it possible for PBT nanocomposites to maintain moderate modulus and high temperature stiffness with increasing temperature, which was also contributed to the enhancement of the HDT values of PBT nanocomposites. Thus, the improvement in the HDT of PBT composites resulted from the enhanced flexural modulus of PBT nanocomposites as well as the increased ability of PBT nanocomposites to retain high stiffness induced by CNT.



Fig. 9. Heat distortion temperature (HDT) of PBT nanocomposites. Reproduced with permission from Ref. (Kim, 2009b). © 2009 Wiley Periodicals, Inc.

3.6 Thermal behavior

The incorporation of CNT into PBT matrix has less effect on the glass transition temperature (T_g) and melting temperature (T_m) of PBT nanocomposites (Table 2). The crystallization temperature (T_c) significantly increased with the introduction of CNT, and this enhancing effect was more pronounced at low CNT content. This result indicates the efficiency of CNT as strong nucleating agents for the crystallization of PBT, suggesting the enhancement of the crystallization of PBT nanocomposites in the presence of CNT. As shown in Table 2, the increase in the T_c of PBT nanocomposites with increasing CNT content, together with the fact that the degree of supercooling (ΔT) for crystallization. Thus, the incorporation of a very small quantity of CNT into PBT can effectively enhance the crystallization of PBT nanocomposites nucleation. Similar observations have been reported for the CNT/polymer nanocomposites, i.e., the accelerated crystallization by the introduction of CNT through heterogeneous nucleation (Kim et al., 2006a; Kim et al., 2007; Kim et al., 2009; Kim et al., 2009; Kim et al., 201).

Materials	Т _g (°С)	$T_{\rm m}$ (°C)	$\Delta H_{\rm m} \left({\rm J} / / {\rm g} \right)$	T _c (°C)	ΔT a (oC)
PBT	56.9	224.4	41.7	176.8	47.6
PBT/CNT 0.5	56.2	224.6	42.4	190.3	34.3
PBT/CNT 1.0	56.7	223.9	43.1	191.4	32.5
PBT/CNT 2.0	57.1	224.3	44.3	192.2	32.1

Table 2. Thermal behaviour of PBT nanocomposites with the CNT content [a The degree of supercooling, $\Delta T = T_m - T_c$]

Wide-angle X-ray diffraction (WAXD) analysis was conducted on the PBT nanocomposites to investigate the effect of the CNT on the structure of the PBT nanocomposites. WAXD patterns of PBT nanocomposites are shown in Figure 10. For pure PBT, strong diffraction peaks observed at near 15.8°, 17.1°, 20.4°, 23.1°, and 25.0°, respectively, were assigned to the (0-11), (010), (011), (100), and (1-11) reflections, indicating the α -form of PBT crystals with a triclinic configuration (Fakirov, 1993). The characteristics peaks of pure PBT were also observed in PBT nanocomposite and the position of their peaks remained almost unchanged with the introduction of CNT, despite some changes in the peak intensity. This result demonstrates that the incorporation of CNT into PBT matrix does not change the crystal structure of PBT nanocomposites. The crystallinity of PBT nanocomposites was slightly increased with the introduction of CNT, which can be explained by the supercooling temperature. For PBT nanocomposites, CNT acts as a strong nucleating agent in PBT matrix, and the crystallization temperature shifts to higher temperature, implying that the supercooling of PBT nanocomposites decreased with the introduction of CNT (Table 2). When polymers crystallized with less supercooling, it crystallized more perfectly than with more supercooling (Cheng & Wunderlich, 1988) and thus, the crystallinity of PBT nanocomposites slightly increased with the introduction of CNT.

3.7 Thermal stability and thermal decomposition kinetics

Thermal stability of polymer nanocomposites plays a critical role in determining the limit of working temperature and the environmental conditions for use of polymer nanocomposites, which is closely related to their thermal decomposition temperatures and decomposition



Fig. 10. Wide-angle X-ray diffraction (WAXD) patterns of (A) pure PBT and (B) PBT/CNT 2.0 nanocomposites. Reproduced with permission from Ref. (Kim, 2009b). © 2009 Wiley Periodicals, Inc.

rates (Nair, et al., 1995). The TGA thermograms of the PBT nanocomposites with CNT content are shown in Figure 11A, and the results are summarized in Table 3. TGA curve of the thermal decomposition for pure PBT exhibited only one dominant decline of the residual weight, indicating the random scission of PBT main-chains as the prevailing decomposition reaction (Vijayakumar & Fink, 1982). The patterns of TGA curves for PBT nanocomposites are similar to that of pure PBT, indicating that the thermal decomposition of PBT nanocomposites primarily stems from PBT. The incorporation of CNT into PBT matrix can increase the thermal decomposition temperatures and the residual yields of PBT nanocomposites, indicating that the presence of CNT can lead to the stabilization of PBT matrix, resulting in the enhanced thermal stability of PBT nanocomposites. The CNT can effectively act as physical barriers to hinder the transport of volatile decomposed products out of PBT nanocomposites during thermal degradation process, leading to the retardation of the weight-loss rate of thermal degradation products as well as the thermal insulation of polymers in the nanocomposites (Kashiwagi et al., 2002).

Materials	T ₅ (°C)	T ₁₀ (°C)	$T_{\rm dm}$ (°C)	IPDT a (°C)	W _R ^b (°C)
PBT	371.3	378.2	400.9	481.0	5.82
PBT/CNT 0.5	372.9	380.2	402.8	499.8	6.81
PBT/CNT 1.0	373.9	381.1	404.4	507.5	7.32
PBT/CNT 2.0	374.8	382.7	407.5	529.9	8.51

Table 3. Thermal stability of PBT nanocomposites with the CNT content [a The intergral procedure decomposition temperature, $IPDT = A \cdot K(T_f - T_i) + T_{i\nu}$ where A is the area ratio of total experimental curve divided by total TGA curves, K is the coefficient A, T_i is the initial experimental temperature, and T_f is the final experimental temperature; b The residual yield in TGA thermograms at 800°C under N₂]



Fig. 11. (A) TGA thermograms of PBT nanocomposites. (B) Plots of $\ln[\ln(1 - \alpha)^{-1}]$ versus θ as shown for PBT nanocomposites. Reproduced with permission from Ref. (Kim, 2009b). © 2009 Wiley Periodicals, Inc.

The TGA kinetic analysis was conducted on PBT nanocomposites to clarify the effects of CNT on the thermal stability of PBT nanocomposites. The thermal decomposition temperatures and decomposition kinetic parameters, including the thermal decomposition temperatures at 5 and 10% of the weight loss (T_5 and T_{10}), the temperature at maximum rate of the weight loss (T_{dm}), the integral procedure decomposition temperature (*IPDT*), and the activation energy for decomposition (E_a) are in common use to characterize the thermal stability of polymer nanocomposites (Park & Cho, 2000). As shown in Table 3, the thermal stability factors, including T_{d5} , T_{d10} , T_{dm} , and *IPDT*, of PBT nanocomposites were higher than that of pure PBT and they tended to increase with the CNT content. This result indicated that the incorporation of a very small quantity of CNT into PBT could substantially improve the thermal stability of PBT nanocomposites, and the thermal volatilization of PBT could be retarded in the presence of CNT during thermal decomposition. Because PBT molecular chains were more difficult to thermally decompose with the introduction of CNT, the residual yields of PBT nanocomposites also slightly increased with the CNT content. For PBT nanocomposites, the introduced CNT to induce protective barriers against thermal decomposition for organic species retarded the thermal decomposition of PBT nanocomposites, resulting from the physical barrier effects induced by CNT acting as the mass and heat transfer barriers (Kashiwagi et al., 2005). As a consequence, the thermal stability of PBT nanocomposites can be enhanced with the introduction of a very small quantity of CNT. Kashiwagi et al. reported that CNT layers exhibited a good barrier effect on the thermal degradation process and could lead to the retardation of the weight-loss rate of thermal degradation products as well as the slow down of thermal decomposition with the introduction of CNT, insulation of polymers in the polymer nanocomposites, resulting in the enhanced thermal stability of CNT/polymer nanocomposites (Kashiwagi et al., 2002). TGA results demonstrate that a very small quantity of CNT is beneficial to act as the thermal decomposition-resistant nanoreinforcing fillers in PBT nanocomposites.

The activation energy for the thermal decomposition (*Ea*) of PBT nanocomposites can be estimated from the TGA thermograms by the Horowitz-Metzger integral kinetic method (Horowitz & Metzger, 1963) as follows:

$$\ln\left[\ln\left(1-\alpha\right)^{-1}\right] = \frac{E_{a}\theta}{RT_{dm}^{2}}$$
⁽²⁾

where α is the weight loss; θ is the variable auxiliary temperature defined as $\theta = T - T_{dm}$, and R is the universal gas constant. The $E_{\rm a}$ values of PBT nanocomposites can be estimated from the slope of the plot of $\ln[\ln(1 - \alpha)^{-1}]$ versus as shown in Figure 11B. The E_a values of PBT nanocomposites were 295.0, 297.5, and 306.2 kJ/mol, respectively. As compared to pure PBT ($E_a = 283.8 \text{ kJ/mol}$), higher E_a values of PBT nanocomposites indicated that PBT nanocomposites were more thermally stable than pure PBT. The presence of CNT in PBT nanocomposites increased the activation energy for thermal decomposition of PBT matrix. The introduction of CNT, effectively acting as physical barriers or protective layers against the thermal decomposition resulted in the enhanced thermal stability of CNT-filled polymer nanocomposites. For PBT nanocomposites, the Horowitz-Metzger analysis demonstrated that the incorporation of CNT into PBT matrix increased the Ea values of PBT nanocomposites, which was related to the enhancement of the thermal stability of PBT nanocomposites. In addition, it can be deduced that the $E_{\rm a}$ values of PBT nanocomposites exhibits a good reliance on describing the thermal decomposition kinetics of PBT nanocomposites, which can be confirmed by the fact that the values of the correlation coefficient (r^2) were greater than 0.99.

The morphology of the residues of PBT nanocomposites containing 2.0 wt% of CNT after thermal decomposition is shown in Figure 12. The PBT nanocomposites exhibited the dispersed structure of CNT in PBT matrix kept after thermal decomposition, despite some collapse or loss of their form. This feature may also contribute to the enhancement of the thermal stability of PBT nanocomposites. This enhancing effect of CNT resulted from high thermal resistance of CNT to increase the energy required for thermal decomposition as well as physical barrier effect against thermal decomposition (Kashiwagi et al., 2005).



Fig. 12. SEM micrograph of the residues of PBT/CNT 2.0 nanocomposites after the thermal decomposition process. Reproduced with permission from Ref. (Kim, 2009b). © 2009 Wiley Periodicals, Inc.

4. Summary and outlook

This chapter describes the fabrication and characterization of poly(butylene terephthalate) (PBT) nanocomposites containing carbon nanotube (CNT). PBT nanocomposites reinforced with a very small quantity of CNT were prepared by a simple melt blending in a twin-screw

extruder to create high performance polymer nanocomposites for practical applications in a broad range of industries. There is significant dependence of the rheological, thermal, and mechanical properties of PBT nanocomposites on the CNT content. The non-terminal behavior of PBT nanocomposites was caused by the nanotube-nanotube or polymernanotube interactions, and the dominant nanotube-nanotube interactions at high CNT content resulted in the formation of the interconnected or network-like structures of CNT in PBT nanocomposites. The presence of a very small quantity of CNT can effectively act as a strong nucleating agent in PBT nanocomposites, resulting in the enhancement of PBT crystallization through heterogeneous nucleation. The mechanical properties of PBT nanocomposites substantially improved with the introduction of CNT, and this enhancing effect was more pronounced at lower CNT content, resulting from the nanoreinforcing effect of CNT with high aspect ratios and large surface areas to allow the efficient load transfer from the polymer matrix to the nanotube. The heat distortion temperature of PBT composites increased with the CNT content, which was related to the enhanced flexural modulus of PBT nanocomposites as well as the increased capability of PBT nanocomposites to retain high stiffness induced by CNT. The incorporation of CNT into PBT matrix increased the activation energy for thermal decomposition, and led to the enhanced thermal stability of PBT nanocomposites, resulting from physical barrier effects of CNT against thermal decomposition. Future development of PBT nanocomposite containing CNT for targeted applications in a broad range of industry will be performed by balancing high performance against their multiple functionality and manufacturing cost.

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Epoxy-based Carbon Nanotubes Reinforced Composites

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1. Introduction

Epoxy or polyepoxide is a thermosetting epoxide polymer that cures (polymerizes and cross-links) when mixed with a curing agent or "hardener". Most common epoxy resins are produced from a reaction between epichlorohydrin and bisphenol-A. Figs. 1 and 2, respectively, show the molecular structure and 3-D model structure of bisphenol-A based epoxy resins. In 1936, bisphenol-A based epoxy resins were first jointly synthesized by Dr. Pierre Castan of Switzerland and Dr. S.O. Greenlee in the United States. Dr. Castan's work was licensed by Ciba, Ltd. of Switzerland, and Ciba went on to become one of the three major epoxy resin producers worldwide [May, 1987].

Epoxy resin is most commonly used as a matrix for advanced composites due to their superior thermal, mechanical and electrical properties; dimensional stability and chemical resistance. Epoxy surface coatings are among the most widely used industrial finishes and provide superior adhesion, flexibility and corrosion resistance when applied to metallic substrates [Jones, 1996]. Epoxy resins are also used with various curing agents, diluents and modifiers to create products with an almost unlimited range and variety of performance properties [The epoxy book, 2000].

Epoxy resins are widely used as high-grade synthetic resins, for example, in the electronics, aeronautics and astronautic industries [Morena, 1988; Nijuguna et al. 2007]. Depending upon the exact application, sufficient matrix conductivity is needed to provide electrostatic discharge or electromagnetic-radio interference shielding [Barrau et al., 2003]. However, epoxy resins are electrical insulators, and the widespread use of the epoxy resins for many high-performance applications is constrained because of their inherent brittleness, delamination and fracture toughness limitations. There were quite a few approaches to enhance the properties of epoxy resins which included: (i) chemical modification of epoxy backbone to make it more flexible, (ii) increasing the molecular weight of epoxy, (iii) lowering the cross-link density of the matrix and (iv) incorporation of a dispersed toughened phase in the cured polymer matrix [Dirlikov et al., 1996; Oh et al. 1996; Sue et al., 1996, Millhaupt & Buchholtz, 1996; Kinloch & Guild, 1996]. Though epoxy resins can be toughened effectively, such methods result in a decrease in other desirable mechanical and physical properties. In another approach, micro-sized filler materials have been used to modify the brittle polymers aiming at synergistic improvements in toughness and rigidity. The addition of filler, usually harder than the matrix, generally leads to an increase in Young's modulus and a reduction in the ultimate elongation of the matrix [Sandler et al., 2003]. However, reports show that the toughening efficiency of these micro-sized particles is much lower, as the rigid particles cannot effectively stop crack propagation [Lee & Yee, 2000].



Fig. 1. (a) Molecular structure of bisphenol-A based epoxy resins. Reproduced with permission from Marcel Dekker Inc., USA.



Red=Oxygen,Ash=Hydrogen, Black=Carbon

Fig. 2. 3-D model structure of bisphenol-A based epoxy resins. Reproduced with permission from Marcel Dekker Inc., USA.

A newly developed strategy offering promising results is to reinforce epoxy matrices with nano-sized organic and inorganic particles such as carbon nanotubes (CNTs), carbon nanofibres (CNFs), nanoclays, metal oxide nanoparticles, etc. [Puglia et al., 2003; Al-Saleh & Sundararaj, 2009; Sinha Ray & Okomoto, 2003; Kim et al., 2008] and make new materials with enhanced properties. The unique properties of the nanoparticles such as nanometric size, high specific surface areas (up to 1000 m²/g) and the possibility of combining them with conventional reinforcements have caused intense research in the field of nanocomposites.

1.1 Carbon nanotubes

Of the various nanofillers used to modify polymer matrices, CNTs have attracted great interest recently as structural reinforcements because of their unique properties. CNTs are the stiffest known fibres which possess a tensile strength of 50-100 GPa and a measured modulus of 1.4 T Pa, which are by far the highest known [Zhu et al., 2003]. In addition, CNTs possess superior thermal and electrical conducting properties varying from metallic to moderate band-gap semi-conductive behaviors depending on their chirality, size and purity. Therefore, it is possible to improve the physical and mechanical properties and electrical conductivity by adding a certain amount of CNTs to the polymeric structures [Lau et al., 2003]. CNTs were first identified by M. Endo and his co-workers in the late 1970s [Oberlin et al., 1976] and caused tremendous interest when S. Iijima published his paper in Nature in 1991 [lijima, 1991]. The synthetic methods for CNTs include the carbon arc-discharge method [lijima, 1991; Kroto et al., 1985], laser vaporization of a graphite electrode [Thess et al., 1996] and the chemical vapour-deposition methods from various carbon precursors [Baker et al., 1972; Yacaman et al., 1993; Hsu et al., 1995; Pigney et al., 1997; Colomer et al., 1998]. CNTs have many structures, differing in length, thickness, spiral types and number of layers; although they are formed from essentially the same graphite sheet [Saito et al., 1992; Zhang et al., 1993; Bernholc at al., 1997; Rao et al, 1996; iijima, 1992]. There are two main types of CNTs: single-walled CNTs (SWCNTs) and multiwalled CNTs (MWCNTs).

SWCNTs: The structure of a SWCNT can be conceptualized by wrapping a one-atom-thick layer of graphite (called graphene) into a seamless cylinder (see Fig. 3). Most SWCNTs have a diameter of close to 1 nm, with a tube length that can be many thousands of times larger. SWCNTs with lengths up to orders of centimetres have been produced [Journet et al., 1997]. MWCNTs: MWCNTs consist of multiple layers of graphite rolled on themselves to form a tube shape. There are two models which can be used to describe the structures of MWCNTs. In the Russian doll model, sheets of graphite are arranged in concentric cylinders. In the parchment model, a single sheet of graphite is rolled in around itself, resembling a scroll of parchment or a rolled up newspaper (Fig. 4) [Dresselhaus, 1996].



Fig. 3. (a) Formation of SWCNT. Reproduced with permission from www.nanotechnow.com and (b) TEM image of SWCNTs.

There are also other two varieties of CNTs generally used for the preparation of composite materials with various polymer matrices. These are double-walled CNTs (DWCNTs) and cup-stacked CNTs (CSCNTs).



Fig. 4. (a) Computer generated MWCNT model. Reproduced with permission from www.nanotech-now.com and (b) TEM image of MWCNTs.



Fig. 5. (a) Computer generated image of DWCNT (www.nanotechweb.org) and (b) SEM images of DWCNTs. Reproduced from Endo et al., 2005.

DWCNTs: DWCNTs are considered as the simplest member of the family of MWCNTs, consisting of two coaxial SWCNTs [Saito et al., 2001; Endo et al., 2005]. DWCNTs have unique physical and mechanical properties due to their special double wall structure compared to those of SWCNTs and MWCNTs [Dai, 2002; Liu et al., 2001]. Figs. 5 (a) and (b), respectively, show the computer generated and SEM images of DWCNTs.

CSCNTs: CSCNT structure provides a hollow tubular morphology, composed of cupshaped carbon units with diameters ranging from 50 to 150 nm and lengths of up to 200 μ m, in contrast with conventional CNTs made up of seamless cylinders of hexagonal carbon network (see Fig. 6). In addition, the availability of reactive edges on the outer and inner surfaces of cup-shaped carbons to chemical functionalization or surface modification will open up new ways to utilize them in electronic, catalytic and photovoltaic applications. The ball milling processes are reported to result in a decrease in the average lengths of pristine CSCNTs (up to 200 μ m) into 7 μ m after 24 h milling [Endo et al., 2005; Endo et al., 2003; Kim et al., 2002; Iwahori et al., 2002]. However, individual cup-shaped carbons with the controlled diameter and size have yet to be obtained.



Fig. 6. (a) Computer generated model of CSCNTs and (b) SEM image of CSCNTs. Reproduced from Iwahori et al., 2002.

CNTs possess unique characteristics relative to the numerous available fillers: amazing mechanical properties, phenomenal electrical and thermal conductivity, nanoscopic size and

high aspect ratio make them the perfect choice in principle to use as reinforcement for polymer composites [Lu, 1997; Salvetat et al., 1999; Srivastava et al., 2003; Buryachenko et al., 2005; Thostenson et al., 2001; Ajayan et al., 2003; Thostenson et al., 2005; Sandler et al., 1999]. This combination of properties can also lead to electrical percolation at low concentrations and has naturally spurred considerable activity in producing value-added multifunctional polymer composites based on CNTs [Winey et al., 2007]. Although the CNT production cost is higher than that of conventional fillers, its low loading is advantageous because the effects on resin properties are minimal and the same processing equipment can be used with neat resins and nanocomposites. These polymer-based nanocomposites are expected to derive high properties at low filler volume fractions due to the high aspect ratio and high surface area to volume ratio of the nano-sized particles [Zhou et al., 2008; Hu et al., 2008; Santos et al., 2008].

In recent years, different types of polymer composites have been synthesized by incorporating CNTs into various polymer matrices such as polyamides [Zhao et al., 2005], polyimides [Cai et al., 2004; Ogasawara et al., 2004], epoxy [Winey et al., 2007; Hu et al., 2008; Liao et al., 2004], polyurethane [Koerner et al., 2005; Kuan et al., 2005], polypropylene [Seo et al., 2004; Li et al., 2004; Seo et al., 2005], polyethylene [Haggenmueller et al., 2006], polyethylene oxide [San et al., 2001], poly(vinyl alcohol) [Shaffer et al., 1999], poly(methyl methacrylate) [Jin et al., 2001], polycarbonate [Postscke et al., 2003], poly(butylene succinate) [Sinha Ray & Okomoto, 2003], polylactide [Chiu et al., 2008], polyaniline [Zing et al., 2008], polypyrrole [Sahoo et al., 2007], polv(N-vinvlcarbazole) [Maity et al., 2007; Maity & Sinha Ray, 2008a ; Maity & Sinha Ray, 2008b], poly(ethylene 2, 6-naphthalate) [Kim et al., 2008], poly(butylenes terephthalate) [Garcia-Gutierrez et al., 2008], poly(p-phenylene benzobisoxazole) [Kumar et al., 2002], glycopolymer [Gao et al., 2007] and others [Fragneaud et al., 2007]. However, the potential of using CNTs as reinforcements has not been realized mainly because of the difficulties in processing and the limitation on load transfer. The tiny size of the nanostructures intensifies their tendency to form agglomerates, and their large surface area per unit volume yields an augmented influence of the interfacial bonding on the effective properties of the composite. Because of the intrinsic van der Waals attraction of the CNTs to each other and high aspect ratio, tubes are held together as bundles and ropes having very low solubility in most solvents. When blended with the polymer, CNTs remain as entangled agglomerates which prevent homogeneous dispersion of the filler into the polymer matrix. Again, the smooth non-reactive CNT surface limits the load transfer from the matrix to nanotubes. Additional processing problem arises due to the increase in viscosity when the CNTs are added directly to the polymer [Zhu et al., 2003]. For CNT-composites, the problem is aggravated by the influence of tube morphology and content of amorphous carbon and metal impurities normally contained in the as-produced CNTs. These impurities, synthesized along with CNTs, are frequently removed (or at least reduced) by oxidative processes, which may lead to structural and morphological changes in the tubes [Martinez et al., 2003; Hiura et al., 1995; Xing et al., 2005]. Given the potential of the CNTs as reinforcement agents, several researchers have aggressively pursued their use in polymer nanocomposites: either thermoplastics or thermosettings [Liu et al., 2004; Andrews et al., 2002; Gryshchuk et al., 2006].

CNT-based epoxy composites are materials of high technological interest because of features such as their mechanical, thermal and electrical properties. A large number of recent works have dealt with CNT-reinforced epoxy. In spite of the aggressive work that has been lately dedicated to this topic, it is widely recognized that the experimental results are still not convergent and continuous research is needed in order to shed light on the development of the composites of the future. Different processes and controversial results were reported on CNT-reinforced composites earlier concerning the improvement of their mechanical, thermal and electrical properties. Thus, the main objective of this article is to report, from the available literatures, the recent progress on the experimental research on CNT-based

2. Epoxy-CNT composites-fabrication and characterization

2.1 MWCNTs-containing epoxy composites

epoxy composites and their properties.

MWCNTs consist of multiple rolled layers (concentric tubes) of graphite. They exhibit unique mechanical as well as electrical properties, which have caused them to be widely studied. This fantastic property of mechanical strength allows MWCNTs to be used as possible reinforcing materials. Just like current carbon fiber technology, MWCNTs reinforce would allow electrically conductive very strong and light materials to be produced. These properties of MWCNTs attracted the attention of scientists in all over the world to incorporate in epoxy matrix for the fabrication of advanced engineering materials. In this section, we reviewed various techniques used to preparae and characterize MWCNTscontaining epoxy composite materials.

2.1.1 Preparative methods and morphological study

Following the first report on the preparation of aligned arrays of MWCNTs by cutting epoxy-CNTs composites by Ajayan et al. [Ajayan et al., 1994], there have been continuous efforts to incorporate CNTs into various types of epoxy resins to fabricate functional composite materials with desirable electrical and mechanical properties. They reported a simple method to produce aligned arrays of CNTs into the epoxy matrix. MWCNTs produced by arc-discharge and purified nanotubes in ethanol were randomly dispersed in a liquid epoxy resin by mechanical mixing with a glass rod. The resin was prepared by mixing epoxy resin (Epon 812) with the curing agents dodecenyl succinic anhydride (DDSA: 12.4 ml) and methyl nadic anhydride (MNA: 9.4 ml) and the accelerating agent, 2,4,6-tris (diaminomethylaminomethyl) phenol (DMP 30: 0.7 ml) by magnetic stirring for 2 h. The composite after evacuation was hardened in capsular shaped blocks for 24 h at 60°C. Low and high magnification transmission electron microscopy (TEM) images of the thin slices cut from the composite showed that the thinner and longer nanotubes were preferentially oriented along the cutting direction, though the thicker tubes and nanoparticles had random orientation. Most of the tubes were adhered to the polymer matrix, and the directional cutting process created shear that induced flow of the tubes. The tubes on the surface were deformed during cutting (due to defect formation) and were oriented unidirectionally on the newly formed surface. The weak interfacial bond between tubes and the matrix was apparent from the unbroken and straightened CNTs after the cutting process which at the same time showed the extraordinary mechanical strength of the tubes.

In 1998, the same group studied the mechanical and load transfer behavior of MWCNTepoxy composites in tension and compression [Schadler et al., 1998]. About 5 wt% of MWCNTs was ultrasonically dispersed in Epon 828 epoxy resin matrix. The composites were cured with triethylene tetraamine hardener by gelling overnight at room temperature (RT) and curing at 100°C for 2 h. The micro-structural analysis of the composite using scanning electron microscopy (SEM) revealed that while the CNTs were poorly distributed, individual tubes were well dispersed in the matrix. Curved and interwoven tubes were observed in the composite showing extreme flexibility.

Sandler and co-workers [Sandler et al., 1999] dispersed untreated MWCNTs in an epoxy matrix using the process developed for carbon black [Schüler et al., 1997]. The matrix used in this study was an epoxy polymer based on bisphenol-A resin (Araldite LY 556) and an aromatic hardener (Araldite HY 932). Weight percentages ranging from 0.0225 to 0.15 wt% of the pristine CVD-grown [Tennent et al., 1992] MWCNTs (diameter 5–10 nm, length a few microns) were first dispersed in ethanol in an ultrasonic bath at RT for 1 h. The solution was then mixed with the resin and stirred for 1 h at 2000 rpm at 80°C. Ethanol was evaporated in a vacuum oven at 80°C for 1 h, and the mixtures were stirred again for 1 h at 2000 rpm. After adding the hardener, the mixtures were stirred at 2000 rpm for 15 min. The resulting epoxy nanocomposite was hardened in a vacuum oven at 140°C for 8 h.

Parts (a) and (b) of Fig. 7, respectively, show the SEM image of the CNT material and magnified transmission light micrograph of the composite sample containing 0.0225 wt% of CNTs. The images show a remarkable improvement in the dispersion of the CNTs in the epoxy resin due to the ultrasound exposure. At these low filler fractions, neither the processing behavior (viscosity) of the matrix nor the surface finish of the samples were adversely affected.



Fig. 7. (a) SEM image of CNT material, as-supplied and (b) magnified transmission light micrograph of the composite sample containing 0.0225 wt % CNTs. Reproduced from Sandler et al., 1999.

Gong et al. [Gong et al., 2000] used a non-ionic surfactant for dispersing CNTs in epoxy polymer matrix. The bisphenol-A epoxy resin with hydroxylated polyamine hardener H-91 and the surfactant polyoxyethylene 8-lauryl ($C_{12}EO_8$) were used for the composite preparation. In a typical procedure, 19.2 mg $C_{12}EO_8$ was dissolved in 0.5 g acetone in a small beaker to which 25.2 mg of MWCNTs was added and magnetically stirred for 15 min at room temperature. Then, 2.0 g epoxy and 0.5 g hardener were added. This produced a viscous suspension. The suspension was stirred for another 15 min until it appeared to be homogeneous. The mixture was poured into a mould and cured at RT overnight, followed by an elevated temperature cure at 80°C for 2 h and 120°C for 2 h. The control samples were made by using the same procedure without $C_{12}EO_8$ or CNTs.



Fig. 8. SEM photographs of CNTs on fracture surfaces of the composite samples: (a) without $C_{12}EO_8$ and (b) with $C_{12}EO_8$. Reproduced from Gong et al., 2000.

The morphology of the fractures surfaces of samples with and without the surfactant were analysed by SEM and results are presented in Fig. 8. CNTs in the composite without surfactant [Fig. 8(a)] appeared to be very long, wavy and lumped together, while the ones with the surfactant [Fig. 8(b)] were more evenly distributed and aligned along one direction. These observations indicated that the CNTs were better dispersed in the polymer matrix in the presence of the surfactant and the load was transferred to the tubes during the fracture process. The surfactant interacted with carbon through the hydrophobic segment, and at the same time, the hydrophilic segment could interact with the epoxy through hydrogen bonding which overcame the van der Waals attractive force between the carbon surfaces in a poor solvent [Everett et al., 1973; Israelachvili, 1992].

To study the deformation micromechanics of CNTs filled epoxy composites using Raman spectroscopy, Cooper et al. [Cooper et al., 2001] synthesized CNT-epoxy composites by adding CNT-ethanol mixture to uncured epoxy resin and then sonicated for 2 h. The solvent was evaporated in a vacuum oven overnight. The hardener was added, and the mixture was stirred well to distribute the nanotubes and again placed in a vacuum oven for about 30 min. The resin was moulded and cured at RT for seven days. The composite was formed by applying the epoxy resin-CNTs mix to the surface of the epoxy beam to give a layer of 0.1 mm thick and was cured at RT for seven days before testing. Unfortunately, authors did not report dispersion characteristics of CNTs in the epoxy matrix.

On the other hand, Cui and co-workers [Cui et al., 2003] examined the influence of incorporation of surfactant during MWCNT-epoxy composite processing. In a typical experimental procedure, the epoxy resin Araldite D (diglycidyle ether of bisphenol) was mixed with an amine type hardener (HY 956) under the ratio 10:2 in weight. The MWCNTs prepared by CVD were purified by high temperature treatment and dispersed ultrasonically in acetone with 2 wt% of surfactant-Tergitol NP 7. The araldite D was added to the MWCNTs dispersed solution and ultrasonicated again for 15 min. The mixture was then mixed for 1 h, at 80°C by shear mixing with a rotating blade. The solvent was evaporated in a vacuum oven, and the mixture was cooled to RT. Polymerization of the mixture was done by stirring with a polymerizing agent at 120°C for 1 h. Two series of composites (with or without the surfactant) were prepared by varying the MWCNTs content from 0.26 to 12 wt%. Optical microscopy images showed a better dispersion of nanotubes in the presence of

the surfactant as reported by Gong et al. [Gong et al.,2000] However, at higher MWCNT content, agglomerates were observed in the matrix.

Other researchers investigated the effect of ultrasonication to disperse CNTs in the epoxy matrix. For example, Lau and co-workers [Lau et al., 2003] different weight fractions of MWCNTs, produced by arc-discharge method, into the epoxy resin (Araldite GY 251) by ultrasonication of resin with ethanol solution of CNTs for 2 h. The composites were dried in vacuum oven for two days to remove air bubbles and the solvent. Hardener (HY 956) was then added to the mixtures at a resin-to-hardener weight ratio of 1:0.23 and sonicated again for 1 h to get uniform nanotube distribution, and the samples were kept in vacuum at RT for 7 days before testing.

The SEM micrographs showed more micro-voids in composite samples at low CNT content when compared to the pure epoxy, which could be a possible reason for the decrease in composite hardness. However, the authors observed that with the continuous increase of the nanotube content, void size decreased (due to the formation of network structure) increasing the hardness property. Local deformation and pull out of CNTs were observed in the load direction.

Like previous authors, Park et al. [Park et al., 2003] also employed the sonication method to disperse CNTs in the epoxy matrix. In their experimental procedure, the MWCNTs (0.1, 0.5 and 2 vol.%) were first sonicated with methanol-based epoxy solution for 2 h, and the sonication was continued for 6 h at 35°C to remove the solvent. The samples were then dried in a vacuum oven at 50°C for 7 days. The morphological study by SEM clearly showed a significant increase in CNT-contact points or network in the polymer matrix with increase in CNT content. However, authors did not report details of morphological study by TEM.

In another report, Wong et al. [Wong et al., 2003] fabricated CNT-epoxy thin film by spin coating technique. Their main objective was to study the interfacial morphology of CNT/epoxy composite. A standard 4-in. silicon wafer was used to spin-coat the mixture of MWCNTs and epoxy resin (Epon SU-8). After curing the composite film system, the substrate was etched from the backside by deep reactive ion etching (DRIE) which left a circular thin film on the rigid substrate with a hole 8 mm in diameter. Extensive examination of the CNT-epoxy interface by TEM indicated that CNTs are in intimate contact with the polymer with no physical gap. No noticeable CNT pull out from the epoxy was observed in the CNT/epoxy slices after microtoming, and most of the CNTs remained in the epoxy, suggesting good adherence of the polymer to CNT. The authors tried to explain the observed CNT-polymer adhesion by proposing mechanical interlocking as a possible mechanism. However, the local non-uniformity along a CNT, such as varying diameter and bends (due to non-hexagonal defects), contribute to mechanical interlocking, and so, extra energy is needed to deform the polymer causing CNT-pull out. A molecular model of CNT with diameter variation embedded in an array of linear polyethylene illustrated this mechanism. (for better understanding refer Fig. 9).

The effect of processing conditions on the degree of dispersion of MWCNTs in epoxy matrix was studied by Sandler and co-workers [Sandler et al., 2003]. The aligned CVD-grown MWCNTs with loading of 0.001–1 wt% were used for composites preparation [Sandler et al., 1999]. For the preparation of composite, a required amount of CNTs were dispersed in a bisphenol-A resin (Araldite LY 556) by shear-intensive mechanical stirring using a dissolver disk. The mixture was then stirred at RT for 1 h at 2000 rpm. After reducing the resin temperature with dry ice in order to increase the viscosity (shear force) the mixture was again stirred for 1 h at 2000 rpm. Finally, the resin temperature was raised to 80°C and



Fig. 9. A molecular model of a CNT embedded in two layers of short linear polyethylene array. Extra energy is needed to pull the CNT through the 'interlock'. A is point of entry and B is near-pullout position. Reproduced from Wong et al., 2003

equilibrated for 10 min. After addition of the hardener at this temperature, the mixtures were stirred for 1 min at 500 rpm followed by 4 min at 50 rpm to allow for a homogeneous dispersion of the hardener and to enhance the nanotube agglomeration process. The moulded composites were cured at 140°C for 8 h.

SEM and optical microscopy images of the fractured composite surface revealed that though the procedure led to very good dispersion of low wt% of aligned CNTs in the polymer matrix, agglomeration occurs from 0.025 wt% onwards. The processing found to be much more difficult with entangled CNTs, as the densely packed tubes increased the viscosity of the resin even at low CNTs content.

In a subsequent work, Park et al. [Park et al., 2004] used oxyfluorinated MWCNTs (synthesized using the CVD process) to reinforce epoxy matrix. The objective was to study the effect of oxyfluorinated MWCNTs surfaces on the mechanical and interfacial properties of resulting composites. In a typical experimental procedure, MWCNTs outer surfaces were functionalized with F₂, O₂ and N₂ gases in a batch reactor made of nickel at a pressure of 0.2 MPa with reaction time of 15 min. Surface analysis results with Fourier transform infrared spectroscopy (FT-IR) and X-ray diffraction (XRD) showed fluorine/oxygen contents and -OH groups on MWCNT surfaces were maximized at 100°C. For the preparation of composite, the epoxy resin (diglycidyl ether of bisphenol A-DGEBA, YD-128) was mixed with 0.5 wt% of treated MWCNTs and sonicated for 3 h at 60°C. After adding the hardener diaminodiphenylmethane (DDM), the mixture was stirred thoroughly, degassed to remove bubbles and moulded. The samples were cured for 2 h at 120°C, 2 h at 150°C and finally, 1 h at 200°C. Results show that the mechanical and mechanical interfacial properties of the

resulting composites were improved with increasing F/O content. This indicates that polar groups such as fluorine and oxygen increases the wet-ability of CNTs surface with the expoxy matrix. However, authors did not do any morphological study of composites by electron microscopes.

The cure kinetics of tetraglycidyl-4,4'-diaminodiphenylmethane (TGDDM) [where 4,4'diaminodiphenylsulfone (DDS) used as a curing agent] in presence of MWCNTs were studied by Xie and co-workers [Xie et al., 2004]. On the other hand, Martin and co-workers [Martin et al., 2004] studied the effect of processing conditions on the degree of dispersion of CNTs in the epoxy matrix. In a typical preparative method, the CNTs were mixed with 30 g of resin using a dissolver disk at 2000 rpm for 30 min at RT and for a further 30 min in a bed of dry ice. The samples were equilibrated at a new temperature and cured in a vacuum oven to remove excess air. In the first set of experiments, the temperature of the CNTs-epoxy resin mixture during addition of the hardener was varied as 25°C (sample A), 80°C (sample B) and 140°C (sample C). In the second set, stirring rates during the addition of the hardener were varied at 80°C at the last step to 0 rpm (sample D) and 200 rpm (sample E). For the third set of experiments, curing temperature was varied to 80°C (sample F) and 110°C (sample G).



Fig. 10. Transmission light micrographs of 0.01 wt% composites processed at different conditions (a) stirred at 50 rpm at RT, (b) stirred at 50 rpm at 80 °C, (c) stirred at 50 rpm 140 °C, (d) stirred at 0 rpm at 80 °C, (e) stirred at 200 rpm at 80 °C, (f) cured at 80 °C and (g) cured at 110 °C. Scale bar is in cm. Reproduced from Martin et al., 2004.

Transmission light microscopy was used to verify the quality of dispersion and micrographs are presented in parts (a-g) of Fig. 10. From the images it was observed that the CNTs remained well dispersed until the hardener was added. Local aggregation started with the addition of hardener. The good dispersion of CNTs without the hardener was explained with electrostatic stabilization and this theory is well known in the case of colloids [Hunter et al., 1987]. The surface of the nanotubes was observed to be negatively charged [Prasse et al., 1987; Martin et al., 2004] which acted as a surface layer preventing aggregation. The addition of a hardener with an ionic strength different from that of the pure resin decreased the dispersion stability favouring cluster formation. Agglomeration at higher temperature led to finer and more evenly distributed tubes consistent with higher nucleation rate and lower barrier to aggregation [Fig. 10(a), (b) and (c)]. The nanotube network formation was also influenced by the curing temperature. Of different curing temperatures (80, 110 and 140°C) used, 110°C led to a more homogeneous dispersion.

In a subsequent report, the effect of amine functionalization of CVD-grown MWCNTs on different properties of epoxy resin was investigated by Gojny et al. [Gojny et al., 2004]. The epoxy resin Ruetapox LV 0164 was hardened with a poly-ether amine hardener Jeffamine T-403. Composites with non-functionalized and amino-functionalized nanotubes containing 0.05–0.75 wt% MWCNTs were prepared. For the synthesis of composites, the raw CNTs were first purified by oxidation and then surface modified by amine functionalization. Theses tubes were manually mixed into the hardener, sonicated for 20 min at 30% amplitude, mixed with the epoxy resin and again sonicated for 10 min. Finally, the composites were cured for 5 h at 80°C followed by 3 h at 130°C in vacuum for post curing.



Fig. 11. TEM-image of the dispersion of catalytically grown CNTs in an epoxy matrix. Reproduced from Gojny et al., 2004.

The TEM analysis of the sample (refer Fig.11) showed very good dispersion of functionalized nanotubes in the polymer matrix. The SEM images of the fractured surface of composites prepared in different methods revealed that suspending nanotubes in a curing agent like polyetheramine leads to homogeneous stable dispersion. The resulting composite neither showed agglomeration nor a fracture pattern. This indicates the presence of strong interfacial interactions between the CNTs surfaces with epoxy matrix.

Among the various methods, the effects of electric fields on CNTs dispersion in epoxy matrix during curing have also been investigated [Martin et al., 2005]. In a typical preparative method, 0.01 wt% CVD-grown MWCNTs (OD = 50 nm) were dispersed in about 15 g of bisphenol-A epoxy resin for 60 min at RT using a dissolver disk, rotating at 2000 rpm. The mixture was equilibrated at 60°C for a 10 min stirring at 2000 rpm, and then

the hardener (Araldite HY 932) was added (at 32/100 hardener/resin ratio). The mixture was stirred again for 1 min at 60°C at 500 rpm, and then left standing for 4 min to remove excess air. The composite was moulded and cured at 80°C for 4 h. Throughout the full curing cycle, D.C. and A.C. fields of 50, 100 and 200 V/cm were applied to induce the formation of aligned conductive nanotube networks between the electrodes.

The *in situ* transmission optical micrographs of composite showed that during the application of D.C. electric field, the CNTs moved towards the anode under electrophoresis due to the negative surface charges. The accumulation of nanotubes created high field strength, further adsorbing more and more tubes, forming dendritic agglomerates from 5 min curing time which increased with curing time. In A.C. fields, more uniformly aligned nanotube agglomeration was achieved with the same effect in bulk composites.

To study the effect of incorporation of surface oxidised MWCNTs on the glass transition temperature (Tg) of epoxy matrix, Barrau and co-workers [Barrau et al., 2005] prepared epoxy/MWCNTs composites by blending MWCNTs with epoxy resin. CVD-grown MWCNTs (<3 nm diameter) after acid treatment with HCl were used for composite preparation. CVD-grown MWCNTs containing trapped iron nanoparticles were also used for preparation of MWCNTs-containing epoxy composites [Zilli et al., 2005]. The main purpose of this work was to study the magnetic properties of resulting composites. The epoxy pre-polymer and the curing agent used were DGEBA LY 556 and isophorone-diamine (IPDA HY 2962), respectively. In a typical fabrication process, CNTs (0, 0.03, 0.1, 0.2, 0.4, 0.5 and 1 wt%) with diamine was sonicated in an ultrasonic bath for 30 min. The pre-polymer was then added to the compound, mixed at 700 rpm for 15 min and sonicated again for another 15 min (the amine/epoxy ratio was 1). The mixture was placed in a vacuum and dried for 120 min to eliminate air bubbles. The degassed composite was moulded and cured. The cure schedule was 60 min at 60°C, 60 min at 140°C and 360 min at 190°C. The SEM images of the fractured surfaces of the samples showed increased agglomeration of the CNTs above a threshold weight fraction of 0.4 wt%. Ganguli et al. [Ganguli et al., 2005] and Rajoria et al. [Rajoria et al., 2005] used the same method for the synthesis of MWCNTs containing epoxy composites.

In another article, Liu et al. [Liu et al., 2005] used rubbery and glassy epoxy matrices for dispersing CNTs. The MWCNTs with diameter 30-50 nm and length 1-5 µm were aminetreated with acid and SOCl₂ following the reported procedure [Li et al., 2005; Liu et al., 2003]. Two kinds of aliphatic amine curing agents – α,ω - polypropyleneoxide diamine (Jeffamine D-2000) and glycolitic polypropyleneoxide triamine (Jeffamine T-403)-were used to prepare composites the epoxy resin diglycidyl ether of bisphenol A (Epon 828). To prepare the CNT-epoxy composite, the required amount of functionalized CNTs (1 wt%) was first dispersed in chloroform. The curing agent was then added and sonicated for 1 h. After evaporating chloroform with continuous stirring, a stoichiometric amount of Epon 828 was added to the mixture and stirred for 1 h at 75°C. The mixture was degassed in vacuum for 1 h and moulded. Epon 828/D-2000 samples were cured at 75°C for 3 h and at 125°C for an additional 3 h. The Epon 828/T-403 system was stirred for 15 min at RT, followed by degassing in vacuum for 2 h. The curing was carried out at 80°C for 2 h and 125°C for 3 h. Parts (a) and (b) of Fig. 12, respectively, show the SEM images of fractured surface of 1 wt % f-MWNTs-epoxy resin composites of Epon 828/D-2000 composite and Epon 828/T-403. It is clear from images that the MWCNTs were dispersed homogeneously in the rubbery Epon 828/D-2000 matrix. Strong interfacial bonding was inferred in this case, as the CNTs were of



Fig. 12. SEM images of fractured surface of 1 wt % f-MWNTs-epoxy resin composites: (a) Epon 828/D-2000 based and (b) Epon 828/T-403 based. Reproduced from Liu et al., 2005.

short free length with no pull out. On the other hand, the CNT dispersion was non-uniform in the glassy Epon 828/T-403 matrix, showing poor adhesion. The CNTs' ends were curved but still embedded in the matrix. The non-uniform dispersion of CNTs into the polymer matrix could be due to the high viscosity of the matrix. A different reinforcing effect of CNTs depending on nature of the polymer matrix is apparent from the images. Dong et al. [Dong et al., 2005] also used the same method for the preparation of MWCNTs-containg epoxy composites.

Fidelus et al. [Fidelus et al., 2005] used two different types of epoxy resins: (i) LY 564/hardener: HY 560 and (ii) Epon 815/hardener: Jeffamine T-403 polyetheramine for the fabrication of CNTs containing epoxy composites. In their experimental procedure, the surfactant sodium dodecyl sulphate (SDS) was first dissolved in tetrahydrofuran (THF) and MWCNTs were dispersed in the solution by ultrasonication for 1 h. Epoxy resin was then added under sonication for 4 min. To evaporate the solvent, the mixture was kept at 45°C overnight followed by 1 h in vacuum. The hardener was added (100:27 ratio for LY 564/HY 560 and 100: 43 ratio for Epon 815/T-403) and mechanically mixed with the epoxy/nanotube mixtures. The mixtures were vacuum dried (30-40 min for LY564/HY560 and 90-100 min for LY564/HY560) and moulded. The LY 564/HY 560 samples were cured at 80°C for 10 h or left at RT for 24 h and then cured at 80°C for 2 h. Epon 815/T-403 samples were cured at 125°C for 3 h.

The CNT dispersion was slightly less uniform in the Epon 815 resin when compared to LY 564 from the SEM images. The fracture surface for LY 564 appeared to be rougher, suggesting good wetting of the tubes in the matrix. These results also indicated that different polymer matrices have dissimilar reinforcing effect with CNTs.

To study the effect of MWCNTs aspect ratio on the properties of final composites, Pumera et al. [Pumera et al., 2006] fabricated MWCNTs/epoxy composites with two different types of MWCNTs. Both types of MWCNTs (CNT-200: length, 0.5–200 μ m; diameter, 30–50 nm; wall thickness, 12–18 nm and CNT-2: length 0.5–2 μ m, diameter 20–30 nm, wall thickness 1–2 nm) were produced by the CVD technique. The purification was accomplished by stirring the CNTs in 2 M HNO₃ at 25°C for 24 h. Epoxy resin Epotek H77A and hardener Epotek H77B were mixed manually in the ratio 20:3 (w/w) using a spatula. CNT electrodes have been produced by loading the epoxy resin, before curing, with different amounts [i.e., 10, 12.5, 15, 17.5 and 20% (w/w)] of CNTs and mixed for 30 min. The composite was cured at 40°C for 1 week.

Fig. 13 shows SEM images for: (A) long-carbon nanotube-based CNT-200-EC electrode, (B) short-carbon nanotube-based CNT-2-EC electrode, and (C) the conventional GEC electrode. Results showed good dispersion of CNTs in the polymer matrix in general when compared to the conventional graphite-epoxy composite (GEC). CNT-2-EC showed more uniform dispersion in the epoxy matrix, while CNT-200-EC revealed sponge-like topography.

In another work, Ganguli et al. [Ganguli et al., 2006] investigated the effect of loading and surface modification of MWCNTs on the fracture behavior of epoxy composites. The epoxy resin was a two-phase SC-15 epoxy resin system, and the MWCNTs were CVD-grown with 10–50 nm diameter and 1–10 µm length, and each had 10–70 graphene layers. The MWCNTs were surface modified both physically and chemically, the details of which are given in Table 1. The chemical modifications of the MWCNTs were done by a method developed by Xie and Wong i.e., acid refluxing with a nitric-sulphuric acid mixture [Xie et al., 2003]. The bifunctional epoxy resin, SC-15 was mixed with MWCNTs (0.05, 0.1, 0.15 and 0.25 wt%) using a high speed-mixing arm at 3500 rpm in the opposite direction of the mixture. The composite samples were cured and moulded in stainless steel moulds.



Fig. 13. SEM images for: (a) long-carbon nanotube-based CNT-200-EC electrode, (b) shortcarbon nanotube-based CNT-2-EC electrode, and (c) conventional GEC electrode. Reproduced from Pumera et al., 2006.

Specimen	Milling	Annealing	Functionalization
MWCNT1	Milled	None	Chem treatment
MWCNT 2	Milled	None	None
MWCNT 3	Raw	None	Chem treatment
MWCNT 4	Raw	None	None

Table 1. Samples used in the study. Reproduced from Ganguli et al., 2006.

The fractured surface morphology of the notched samples from SEM analysis showed ridge formation on all the samples with more fracture for the acid-treated than for the ball-milled sample. The AFM image of the neat resin showed uniform circular indentations formed from the incompatibility of the prepolymer with the hardener during curing. A rougher surface with well dispersed dense MWCNTs was observed for acid-treated composite when compared to the ball-milled sample. Acid treatment was hence found to be advantageous over physical treatment to get better dispersion.
On the other hand, the effect of MWCNT dispersion on the light transmittancy of MWCNTepoxy composites was investigated by Wang et al. [Wang et al., 2006]. The CVD-grown MWCNTs with outer diameters of 20–80 nm were used for composite preparation. The MWCNTs were first acid-treated and followed by refluxed with SOCl₂ in DMF. Triethylenetetramine (TETA) was then used for surface functionalization. The modified and unmodified MWCNTs were added to molten epoxy resin (bisphenol A-epichlorohydrin epoxy resin, E-44) under magnetic agitation at 80°C for 20 min. The suspensions of MWCNTs in epoxy resin were then sonicated at 80°C for 2 h. The black mixture thus obtained was further added to triethanolamine (TTA) hardener and agitated for 3 min. After degassing in a vacuum oven, the mixture was moulded and cured at 100°C for 2 h, followed by post curing at 120°C for 16 h.

Optical microscopy and TEM were used to study the morphology of the composites. The results showed poor dispersion of unmodified CNTs in the epoxy matrix while the modified CNTs showed relatively uniform dispersion with conglomerations in the nm range.

Kim et al. [Kim et al., 2006] modified MWCNTs by acid, amine treatment or plasma oxidation to improve interfacial bonding and dispersion of nanotubes in the epoxy matrix. CVD-grown MWCNTs with average diameter of 13 nm and length of 10 μ m, epoxy resin (YD 128) and hardener (TH 432) were used in the study. The CNTs were purified in a 3:1 65% H₂SO₄/HNO₃ mixture at 100°C for 30 min. The acid-treated CNTs were functionalized with octadecyl amine (ODA) at 120°C for 5 days or irradiated with Ar plasma containing 1% of O₂ for 1 min. Suspensions of untreated CNTs in ethanol or of chemically modified CNTs in ethanol were sonicated for 2 h and slowly dispersed in heated epoxy resin for 1 h. The mixture was kept under vacuum at 80°C for 5 days to evaporate the ethanol. The plasma-treated CNTs were directly mixed with the epoxy resin.

The SEM images of various samples showed poor dispersion of untreated CNTs in the epoxy. The acid- and plasma-treated tubes showed relatively good dispersion when compared to amine-treated CNTs.

Yaping et al. [Yaping et al., 2006] proposed a new method to disperse MWCNTs homogeneously in an epoxy matrix. CVD-grown MWCNTs (diameter 30–100 nm) were first heated with an excess 2.5 and 20 wt% of diethylenetetramine (DETA) ethanol solution for 30 min, washed with ethanol and dried. MWCNTs and MWCNTs-NH₂ (0.2, 0.4, 0.6 and 1.0%) were added to the epoxy resin at 120°C (CYD-128) and dispersed in a high-speed homogenizer of 20,000 rpm for 20 min. The mixtures were degassed at 90°C for 30 min, and an appropriate amount of hardener (amine 593#) was then added at 50°C. After degasification, the mixture was moulded and cured at 60°C for 1 h. The TEM images showed that the modified CNTs were evenly distributed in the substrate of epoxy resin.

In another recent report, Chen et al. [Chen et al., 2006] proposed a two-step acid-epoxy functionalization of MWCNTs coupled with anionic homopolymerization chemistry to build up the epoxy network. CVD synthesized MWCNTs (length 5–15 μ m, diameter 40–60 nm) were acid-treated by refluxing MWCNTs with 250 ml of concentrated 3:1 H₂SO₄/HNO₃ (70%) [Liu et al., 1998] followed by HCl addition [Chen et al., 1998] to obtain COOH-MWCNTs. The esterification of -COOH groups with epoxy monomers phenyl glycidyl ether (PGE) or DGEBA (Epon 828) was carried out in a DMF solution, using triphenylphosphine (TPP) as a catalyst (0.1 mole TPP per mole of epoxy groups). The reaction was performed by refluxing at 150°C under nitrogen for 36 h. After the treatment, PGE-MWCNTs and DGEBA-MWCNTs were thoroughly washed with ethanol, collected with the PTFE membrane and dried in a vacuum oven for 24 h. Various CNT samples (0.5, 1 and 3 wt%)

were dispersed in THF under sonication for 5 min. DGEBA was dissolved in THF (1:1 by volume) in a dual axis high-speed mixer. Both mixtures were blended in the mixer and sonicated for another 5 min. Finally, THF was evaporated in a vacuum chamber at 100°C overnight. 4-dimethylamino pyridine (DMAP) was added to the mixture in a molar ratio of 0.08 mole DMAP per mole of epoxy groups and mixed further 10 min. The final blend was moulded and cured. The curing cycle employed was 3 h at 80°C, 3 h at 120°C and 30 min at 160°C [dell'Erba et al., 2004].

The examination of the composite surface by SEM showed isolated CNT agglomerations with unmodified and acid-treated MWCNTs. PEG and DGEBA modified MWCNTs were dispersed uniformly in the matrix.

Zhang et al. [Zhang et al., 2006] used MWCNTs produced by CVD (10–25 nm diameter, 10–25 μ m length) to prepare nanocomposite with epoxy resin. CNTs were ultrasonicated for 1 h in acetone (0.1 mg/ml) and then for another hour after the addition of epoxy. The acetone was then removed by heating the mixture to 70°C while stirring, followed by evaporation under high vacuum at 50°C for 24 h.

The surface analysed by SEM and TEM confirmed a good adhesion between the CNTs and the epoxy matrix without CNT bending or cracking. Capless CNTs were in the bulk debris with deformed walls. This preparation method seems to align the CNTs in the sliding direction.

Thostenson and co-workers [Thostenson et al., 2006] utilized a calendering approach similar to that developed by Gojny et al. [Gojny et al., 2004] to disperse CVD-grown MWCNTs (15–20 nm diameter, length over 10 μ m) in an epoxy matrix and studied the evolution of the composite structure during processing. MWCNTs were added to the bisphenol-f epichlorohydrin epoxy resin (Epon 862) by hand mixing. The mixture was processed in the three-roll mill consisting of three chrome-plated hardened steel rolls that are 80 mm in diameter, where the speed of the apron roll was set to 250 rpm. The nanotube/epoxy suspension was processed until there was no material left in the feed area between the feed and centre rolls to ensure shear mixing at progressively smaller gap settings of 50, 30, 20, 10 and 5 μ m. The mixture was heated to 50°C in an oven to reduce the viscosity. Curing agent (Epicure W) at a ratio of 26.4/100 was added and mechanically stirred at 500 rpm for 5 min. The resin was then degassed in a vacuum oven for 15 min at 50°C, molded and cured for 6 h at 130°C. Smaller gap settings of 10 and 5 μ m produced highly dispersed CNTs with less agglomeration.

The composite morphology and CNT dispersion were investigated by SEM. Composites processed at 10 μ m showed CNT pull out along the fracture path with tail like CNT structure in comparison with that processed at 5 μ m.

To get a clear understanding of the influence of CNTs incorporation on the performance of epoxy matrix, Zhuang et al. [Zhuang et al., 2006] prepared a series of composites by incorporating MWCNTs (20 µm length, 80 nm diameter) into an epoxy resin. In their study, a low-viscosity epoxy system was used. MWCNTs (0.05%, 0.075%, 0.1%, 0.3%, 0.5% or 1.0%) were dispersed in about 30 ml of acetone by sonication for 10 min. The mixture was poured into the prepared mixture of a novolac epoxy resin (F-51), methyl hexahydrophthalic anhydride (MHHPA) hardener with 4, 6-tris (dimethylaminomethyl) phenol (DMP-30) as accelerator and then processed for 2 h by ultrasonication along with mechanical stirring at about 100 rpm at 60–70°C for 10 min. The prepared mixture was molded, degassed in a vacuum oven at 80°C for 30 min and then heated according to the specified curing schedule. The curing conditions for the prepared composites are given in Table 2.

No.	Cure Process
1	24 h at 80°C
2	3 h at 80°C+24 h at 100°C
3	3 h at 80°C+24 h at 120°C
4	3 h at 80°C+3 h at 120°C +3 h at 150°C
5	3 h at 80°C+3 h at 120°C +3 h at 150°C+3 h at 180°C

Table 2. Different cure conditions for neat epoxy and MWCNT-epoxy composites.. Reproduced from Zhuang et al., 2006.

CNT concentration from 0.5 wt% produced agglomerations, and according to the authors, the CNT content should be smaller to ensure the stable dispersion of the tubes. 0.1 wt% of CNTs was found to be the critical tube content giving homogenous distribution. The fracture surface analysed by SEM of the samples with 0.1 wt% CNTs cured at different temperatures showed different adhesive nature for the CNTs in the matrix. 100–120°C was found to be the optimum. At lower temperature, curing was insufficient, while at higher temperature, bonding was poor due to the difference in thermal expansion coefficient of the epoxy and CNTs.

Sham et al. [Sham et al., 2006] studied the influences of UV/O₃ as well as TETA treatments for the surface functionalization of MWCNTs and dispersion in an epoxy matrix. The MWCNTs (diameter 10–20 nm, length 10–50 μ m, surface area 420 m²/g) were dispersed in acetone via ultrasonication, washed with de-ionized water and dried at 80°C. The MWCNTs were then subjected to UV/O₃ treatment (in a Jelight 144AX-220 UV/O₃ cleaning system) at varying exposure durations from 2 min to 1 h. The UV/O₃ treated MWCNTs were mixed with a TETA solution and sonicated at 60°C for 1 h. The mixture was then rinsed using excess acetone and filtered. The treated MWCNTs were sonicated with DGEBA (Epon 828) for 5 h followed by out gassing in a vacuum oven at 80°C overnight. A stoichiometric amount of curing agent, metaphenylenediamine (mPDA), was added into the mixture and carefully stirred for 3 min. The mixture was moulded and cured at 80°C for 2 h, followed by post curing at 150°C for 2 h.

The dispersion of CNTs in the polymer matrix was studied by optical microscopy. The CNT surface became more hydrophilic after UV/O_3 treatment and amine functional groups increased the dispersion of CNTs in the matrix. This method gives an alternative approach to oxidize CNTs through damaging process like concentrated acid treatment.

Ci et al. [Ci et al., 2006] evaluated the different reinforcement roles of CNTs in those composites with different matrix stiffness while the curing process is controlled. To understand that, MWCNTs (diameter 20–60 nm) produced by a floating catalyst method [Andrews et al., 1999] were dispersed in acetone by ultrasonication for 1 h, filtered and dried. To prepare CNT-epoxy composite, the 0.5 wt% CNT powder was directly added into a liquid epoxy (bisphenol A-epichlorhydrine), and the solution was mechanically stirred for 5 min to form a homogeneous suspension. 10.7 wt% of an epoxy hardener (triethylenetetramine) was mixed into the suspension and softly stirred for about 2 min. The mixture was placed in a vacuum chamber for about 30 min. Finally, the suspension was moulded and cured for 48–72 h. A series of matrices with different stiffness were prepared by changing the epoxy/hardener ratio and the curing time. High magnification SEM images of soft and stiff matrices showed CNT pull out from the fracture surface. In the soft matrix, good interfacial bonding was observed between the CNTs and the matrix. The results indicated that CNTs have different reinforcing roles for the same polymer depending on the stiffness of the matrix.

Moisala and co-workers [Moisala et al., 2006] reported the use of 80 μ m long CVD-grown MWCNTs [Singh et al., 2003] (0.005-0.5 wt%) in an epoxy system consisting of a bisphenol-A resin (Araldite LY 556) and an aromatic amine hardener (Araldite XB 3473). The composites were made by the high-shear mixing procedure published by Sandler et al [Sandler et al., 2003].

Vacuum-assisted resin transfer moulding (VARTM) process was also used to fabricate epoxy-based composites [Qui et al., 2007]. In a typical processing, pristine and functionalized MWCNTs were infused through and between glass-fibre (A1010 uni-warp knitting glass fibre) tows along the through-thickness direction (refer Fig. 14). MWCNTs were refluxed with a mixture of HNO_3/H_2SO_4 for 30 min, washed with distilled water and filtered. Functionalized MWCNTs were dispersed ultrasonically in the curing agent Epicure W followed by addition of Epon 862. CNT-dispersed resin fluid was infused into the layers of fabric, and the impregnated fibre cloth (pre-preg) was laid up to fabricate composite parts through conventional VARTM.



Fig. 14. Illustration of through-thickness reinforcement by CNTs: (a) one ply fabric and (b) one ply fabric impregnated by MWCNT-resin. Reproduced from Qiu et al., 2007

The wetting and dispersion effects of the MWCNT-resin fluid in the glass fabrics examined by optical microscopy showed successful impregnation in the layered fabrics with CNTs (acid-treated CNTs gave better results) both in inter- and intra-tow arrears. Similar method was also used by Lee et al. [135] for the fabrication of epoxy composites.

CNTs-containing epoxy composites were fabricated by using four different processing conditions, as listed in Table 3 [Li et al., 2007; Ma et al., 2007]. SEM images showed large agglomerated from Conditions A and B whereas these agglomerates were almost completely absent for the composites produced by Conditions C and D. Silane functionalized CNTs (condition D) were dispersed more uniformly, confirming much better dispersion of CNT in epoxy matrix. The optical microscope images showed CNT agglomerates within small localized area for Condition A. For Condition B, the CNT agglomerates covered a larger area. Though the disentanglement was satisfactory for Condition C, the dispersion was poor. The surface treatment provided in Condition D reduced the re-agglomeration and gave a good dispersion state for the CNTs. TEM images showed that there was a systematic reduction in the packing density or "degree of entanglement" that occurred in the order of Conditions A–D, and the corresponding aspect

ratios decreased because of the gradual breakage of CNTs. This article highlighted the importance of silane treatment for improved interfacial interactions and CNT dispersion in epoxy matrix.

Condition	Dispersion Method
А	As received CNT+ epoxy shear mixing for 30 min at 3000 rpm
В	CNTs dispersed by ultrasonication for 1 h in acetone + epoxy
	Ultrasonication for 2 hat 60°C
С	UV/O_3 treatment of CNT for 1h and ultrasonication for 2h in
	acetone+ epoxy
	Shear mixing for 30 min at 3000 rpm
D	CNTs were ball milled for 2h ultrasonicated in toluene for 1h
	UV/O_3 treatment for 2h, followed by Silane treatment [202] + epoxy
	Ultrasonicated for 2 hat 60°C

Table 3. Processing conditions used to disperse CNTs. Reproduced from Li et al., 2007.

In a similar type of work, Chen et al. [Chen et al., 2007] described the influence of different dispersion methods of CNTs in epoxy resin. The MWCNTs (diameter 10-30 nm, length 5-15 μ m, surface area 40–300 m²/g) were dried at 100°C for 2 h and were crushed with a mortar for 10 min before mixing (untreated). The dried CNTs were mixed with a HNO₃ solution (4 mol/l) was boiled at 100°C for 1-2 h while stirring at 300 rpm, washed and dried (acidtreated). The acid-treated CNTs were sonicated in a solution of the coupling agent 3glycidyloxypropyltrimethoxsilane (GLYMO) in acetone (13.6 mol/L) (the weight ratio of coupling agent to CNTs was 1:10 until all the solution was completely evaporated (functionalized). A dual asymmetric centrifuge (speed mixer) was used to mix the CNTs into the hardener or the resin (the resin to hardener ratio was 1:4). The other dispersion methods used were sonication and hand mixing. The mixture was then moulded and cured by heating from 20 to 60°C in 2 h, heating from 60 to 80°C in 2 h and holding at 80°C for 4 h. Zhou et al. [Zhou et al., 2007; Zhou et al., 2008] used a high intensity ultrasonication to process the MWCNT-epoxy composite. Pre-calculated amounts (0-0.4 wt%) of MWCNTs (length 3-10µm, diameter 30-50 nm) and Epon 862 resin were mixed together under high intensity ultrasonication for 1 h on pulse mode, 50 s on/ 25 s off along with ice-cooling. Epicure W (100:26 resin: hardener) was added to the modified resin and mixed using a highspeed mechanical stirrer for about 10 min. The liquid was preheated to 80°C in a vacuum oven for 30 min to reduce its viscosity, molded and cured for 4 h at 120°C.

The SEM images showed that ultrasonic cavitation is an efficient method of infusing CNTs into epoxy resin when CNT weight fractions are lower than 0.3 wt%. CNTs uniformly dispersed in the matrix prevented crack propagation and increased surface roughness. Above the 0.3 wt%, CNTs agglomerated.

In another report, García and co-workers [García et al., 2007] manufactured epoxy nanocomposites by wetting as-grown arrays of vertically grown CNTs (synthesized by CVD) by the submersion method. Two grades of SU-8 UV-curing thermoset epoxy (Microchem 2000.1 and 2025) were selected to prepare the composites. The substrate with CNT pillars was inverted on a stage above a reservoir containing the SU-8 resin. The substrate was then lowered until the pillars contacted the surface of the reservoir. The CNT pillars were soaked for 2 min, and subsequently the SU-8 was cured by the standard process: pre-baking at 65°C for 2 min and at 95°C for 5 min, UV curing for 90 s, post-baking

for 1 min at 65°C and 3 min at 95°C and a final post-baking step at 135°C for 24 h. The regularity of the contraction and the vertical alignment of the CNTs following wetting and curing were revealed by the SEM images. The wetting results showed that the capillarity effect wets CNTs with polymers having viscosities similar to resins used as matrices for traditional composite materials.

On the other hand, Tseng et al. [Tseng et al., 2007] proposed a novel method for the preparation of epoxy composite through the use of functionalization of MWCNTs by plasma treatment and maleic anhydride (MA). CVD-grown MWCNTs were purified by HCl refluxing and oxidation at 600°C. Then the MWCNTs were subjected to plasma treatment [Tseng et al., 2006a, Tseng et al., 2006b]. MA with a concentration of 0.1 M dissolved in toluene was injected into the reactor to graft onto the MWCNTs surfaces at 50°C for 3 h (CNTs-MA). The CNTs-MA were washed by toluene, centrifuged and dried at 70°C overnight. For the preparation of the CNTs-MA-epoxy composites, first, CNTs-MA were added into the diamine curing agent, N,N'-bis (2-aminopropyl) polypropylene glycol, and the mixture was shear mixed for 2 h and sonicated for another 15 min. Subsequently, Epon 828 resin was added and further shear mixed at 80°C for 30 min. Finally, the resulting mixture was outgassed in a vacuum oven for 2 h and then moulded and cured. The curing cycle was 80°C for 2 h, 120°C for 2 h and 140°C for 4 h.

The SEM and TEM images of fractured surfaces of the un-functionalized CNTs (u-CNTs) based epoxy composites showed non-uniform dispersion and formation of agglomerates for untreated CNTs (u-CNTs), while the CNTs-MA system showed good homogeneity and dispersion with CNTs tightly held to the matrix.

Bekyarova et al. [Bekyarova et al., 2007] used electrophoresis for the selective deposition of MWCNTs on woven carbon fabric. The CNT-coated carbon fibers (CF) panels were subsequently infiltrated with epoxy resin using VARTM to fabricate multiscale hybrid composites. CVD-produced MWCNTs (length 2-6 μ m) were refluxed with nitric acid to functionalize them with –COOH groups and were dispersed in water by ultrasonication to obtain dispersions of 0.05 mg/mL. For the electrophoretic deposition, carbon fabric IM7 was fixed in a stainless steel frame, and two stainless steel plates were positioned on both sides as counter electrodes. The carbon fabric was immersed in the nanotube dispersion, and a positive potential of 10 V/cm was applied to the CF. The CNT-CF preforms were infiltrated with epoxy (Epon 862) mixed with the curing agent (Epikure W) using VARTM. After the infiltration of epoxy, the composites were cured for 6 h at 130°C.

From the SEM images, the MWCNTs were found to be deposited as individual tubes with some tubes protruding from the CF surface. The examination of the interface between the CF matrix and the CNTs showed that the CNTs were strongly attached to both the CF and the epoxy matrix.

Sandoval et al. [Sandoval et al., 2007] dispersed controlled amounts of MWCNTs in stereolithography layered (SL) epoxy-based resins. Commercially available epoxy-based SL resins – DSM Somos[®]WaterClearTM and WaterShedTM – were used as the composite's matrix materials. MWCNTs prepared by CVD (diameter 15-45 nm, length 5-20 µm, surface area ~220 m²/g) were purified by means of acid etching and directly seeded in the SL resins to the desired concentrations by means of shear and ultrasonic dispersion for 1 h. The nanocomposite was poured into a vat to manufacture sample parts by selectively curing it to a prescribed geometry using standard SL manufacturing in the multi-material SL machine.

The SEM image taken from the down-face of the sample showed a "winkling effect" which never existed in the pure SL resins, whereas the upper surface was smooth. TEM results

showed affinity between the composite's constituents and strong interfacial bonding effects (buckled nanotubes).

Yuen et al. [Yuen et al., 2007] prepared MWCNT-epoxy composites with CVD-grown MWCNTs (diameter 40–60 nm, length 0.5–40 μ m, surface area 40–300 m²/g). A DGEBA type epoxy resin was dissolved in acetone. The CNTs were also dispersed in acetone. The two solutions were mixed, 4,4'-diaminodiphenyl sulfone solution (curing agent) was added, and the blend was stirred thoroughly. Solvent was removed completely at 40°C. The composite was cured at 150°C for 4 h, followed by post curing at 180°C for 1 h. SEM images showed that the CNTs were mostly buried inside the epoxy matrix with aggregation of some of the CNTs.

Camponeschi et al. [Camponeschi et al., 2007] investigated the effect of orientation and alignment of MWCNTs embedded in different epoxy polymer matrices [Aeropoxy (AP) and Coldfix] under an external magnetic field. The CNTs were dispersed in the resin through ultrasonication. TEM images revealed that CNTs are aligned in the direction of applied magnetic field in the case of AP systems whereas CNTs in the CF system showed various regions of local alignment not necessarily in the field direction.

For the preparation of MWCNTs containing epoxy composites, Abdalla et al. [148] and Shen et al. [Shen et al., 2007] used different amino-functionalized MWCNTs, whereas Kovacs et al. [Kovacs et al., 2007] employed a master batch approach. In a typical preparative method, a master batch of epoxy resin containing a high nanotube concentration was prepared with a dissolver disk rotating at 2000 rpm for 2 h at RT. An appropriate amount of hardener (mixing ratio of 23:100 parts per weight of hardener versus resin) was added and subsequently processed in three different ways. The first sample set was stirred at 500 rpm for 10 min at 80°C (referred to as slow stirring, SS). The second and third sets of samples were stirred at 500 rpm for 10 min at 80°C (medium stirring, MS) and 2000 rpm 15 min at room temperature (fast stirring, FS). The filler concentration in the remaining master batch was then lowered by adding pure resin and again stirred for 30 min at 2000 rpm. All samples were cured in an oven at 120°C overnight.

Fig. 15 shows light microscopy images (7.5 mm width and 5.5 mm height) of 0.5 mm thick samples from each preparation method (rows) and with different nanotube concentrations (columns). The microscopy images of various samples showed gradual development of CNT network to a superstructure in all the processing conditions. Above 0.2 wt% of CNTs, all samples showed homogeneous CNT dispersion.

Yaglioglu et al. [Yaglioglu et al., 2008] presented a process for transfer-printing films and arrays of patterned microstructures by incorporating vertically aligned CNTs (VA-CNTs) in a layer of conductive epoxy. VA-CNTs were deposited on a substrate coated with patterned catalyst by the CVD method. A copper substrate was coated with a thin layer of two parts of isotropic conductive epoxy (Loctite 3888) consisting of silver paste and a hardener. The substrate was brought in contact with the CNT column, a gentle vertical pressure was applied and the assembly was cured at 150°C for 30 min. The copper substrate was then manually separated from the silicon substrate, and the CNT columns were transferred to the copper substrate, owing to the relatively strong adhesion with the epoxy compared to the weak adhesion to the growth substrate.



Fig. 15. Light microscopy images (7.5 mm width and 5.5 mm height) of 0.5 mm thick samples from each preparation method (rows) and with different nanotube concentrations (columns). Reproduced from Kovacs et al., 2007.

Sample	Sequence of addition of constituents	Mixing speed (rpm)	Mixing time	Curing temperature and time	Mixer
А	(1) Epoxy+MWCNT (2) (1)+hardener	(1) 720 (2) 80	(1) 1 h (2) 10 min	(2) 80°C, 2 h	Stirrer
В	(1) Epoxy+ethanol+MWCNT (2) (1)+hardener	(1) 720 (2) 80	(1) 1 h (2) 10 min	(1) 80°C, 2 h (2) RT, 48h	Stirrer
С	(1) Epoxy+ethanol+MWCNT (2) (1)+hardener	(1) 720 (2) 80	(1) 1 h (2) 10 min	(1) 80°C, 2 h (2) 80°C, 3 h	Stirrer
D	(1) Epoxy+MWCNT (2) (1)+hardener	 (1) 2000 (2) 2000 	(1) 1 min (2) 1 min	(2) 80°C, 3 h	Planetary mixer
Е	(1) MWCNT + Epoxy (2) (1)+hardener	 (1) 2000 (2) 2000 	(1) 4 min (2) 1 min	(2) 80°C, 3 h	Planetary mixer
F	(1) MWCNT + Epoxy (2) (1)+hardener	 (1) 2000 (2) 2000 	(1) 4 min (2) 1 min	(2) 80°C, 3 h	Planetary mixer
G	(1) Epoxy+hardner (2) (1)+MWCNT	(1) 2000 (2) 2000	(1) 20 s (2) 1 min	(2) 80°C, 3 h	Planetary mixer
Н	(1)Epoxy+hardner (2)+MWCNT	(1) 2000 (2) 800	(1) 20 s (2) 1 min	(2) 80°C, 3 h	Planetary mixer

Table 4. Processing conditions for various samples. Reproduced from Hu et al., 2008. studies by SEM showed no noticeable difference for fractured surfaces of various samples indicated that processing methods had no effect on morphology.

An in situ polymerization process was used by Hu et al. [Hu et al., 2008] for the fabrication of CNT-epoxy composites. In this study, an insulating bisphenol-F epoxy resin (jER806) with an amine hardener (Tomaido 245-LP) was used. Two kinds of mixing machines – a 4-bladed propeller stirrer with the highest rotation speed of 720 rpm and another planetary mixer with two rotation axes – were used in experiments. Eight samples with 2 wt% MWCNTs loading were prepared under different conditions. For all samples, the ratio of epoxy resin to the hardener was 5:3. The processing conditions are summarised in Table 4.



Fig. 16. SEM images of: (a) CSD/epoxy and (b) CMW/epoxy composites showing tube dispersion. Reproduced from Perez et al., 2008.

Like Pumera et al. [Pumera et al., 2006], Pèrez and co-workers [Pèrez et al., 2008] also studied the effect of aspect ratio (length/diameter) of MWCNTs on epoxy matrix reinforcement. CVD-grown CNTs of two different morphologies were used for the preparation: CSD (diameter 3–170 nm, length 5–9 μ m) and CMW (diameter up to 45 nm, length 30 μ m). The aspect ratio (L/d) of the CMW nanotubes was approximately 17 times larger than that of the CSD ones. First, the desired amount of tubes was dispersed in ethanol for 2 h at RT using an ultrasonic bath. The ethanol/tubes solution was then mechanically mixed with the epoxy resin (Epon 828) at 80°C for 2 h using a magnetic stirrer. The ethanol was then fully evaporated in a vacuum oven at 80°C. The resin/tubes mixture was again stirred for 1 h at 75°C under mechanical agitation. The curing agent *m*-phenylenediamine (mPDA) was then added into the resin under agitation at 75°C, moulded and cured for 2 h at 75°C followed by 2 h at 125°C.

SEM images [refer Fig. 16 (a) and (b)] showed relatively good dispersion for CSD tubes. The shorter length CMW tubes appeared to be agglomerated. Authors believe the high viscosity of the CMW/ethanol mixture which is unfavourable for the composite processing and dispersion.

Yeh et al. [Yeh et al., 2008] reported the fabrication and mechanical properties of MWCNTepoxy composites by the hot press method. MWCNTs (diameter 20–40 nm, length 5–15 μ m) were used as the reinforcement in the epoxy E120-H100. The epoxy was first mixed with the hardener completely, and the mixed compound was put in an oven at 60°C for 5 min. Different weight percentages (0–5 wt%) of MWCNTs were added to the epoxy compound and mixed by a magnetic stirrer for 10 min at 60°C. The composite was kept in the oven at 60°C for another 5 min to increase its viscosity and then hot-pressed at 80°C under pressure (150 psi) for 2 h. Topographical results from SEM revealed good adhesion between the CNTs and the epoxy matrix. Li and co-workers [Li et al., 2008] used both CNTs and graphite nanoplatelets (GNPs) for the fabrication of epoxy based composites. GNPs with average thickness and diameter of 4.5 and 46 μ m, respectively were produced from graphite-intercalated compound and MWCNTs (diameter 10–20 nm, length 10–50 μ m) were prepared by CVD. The CNTs and GNPs were exposed to ultraviolet (UV) light for 20 min and an ozone environment for 5 min to introduce oxygen-containing functional groups on their surfaces. Treated CNTs were sonicated in acetone for 4 h. Epon 828 epoxy was added and mixed via sonication for 2 h. The treated GNPs were subsequently added and mixed using a high shear mixer for 30 min at 3000 rpm. Ultrasonication for 1 h at 80°C followed to further break the agglomerates. The mixture was out-gassed at 80°C for 2 h, and a curing agent (1,3-phenylenediamine) was added to the mixture in the ratio of 14.5/100 by weight. The composite was moulded and cured at 80°C for 2 h, followed by post-cure at 150°C for 3 h. Several different combinations of CNT/GNP hybrid nanoreinforcement contents were added into the epoxy matrix, with the CNT contents ranging 0–1.0 wt% while the total filler content was maintained at 2 wt% loading.

Santos et al. [Santos et al., 2008] investigated the nanocomposite prepared from CVD-grown MWCNTs (diameter 10-40 nm, length 5-20 μm, surface area 136 m²/g), XR1555 epoxy resin and HY-951 Aradur hardener. MWCNTs were suspended in a 1 wt% SDS solution [Connel et al., 2002], and the mixture was ultrasonicated for 90 min. The suspension was centrifuged, and acetone was added to the supernatant to flocculate and remove nanotubes from the suspension. The CNTs were dispersed in the epoxy resin with simultaneous low mechanical stirring and strong sonication for series 1. Next, the hardener was added to the nanotubeepoxy mixture. For series 2, CNTs were dispersed in acetone and then in epoxy. The mixture was maintained in a vacuum oven at 60°C for 15 h for solvent evaporation, and in sequence, the hardener was added with low mechanical agitation and strong sonication. The samples were moulded and cured as follows: (i) temperature ramp of 1°C/min up to 40°C and kept isothermal for 2 h at 40°C and (ii) temperature ramp of 1°C/min up to 60°C and kept isothermal for 8 h at 60°C. The reaction was completed in a vacuum stove for 7 days at 30°C. The successful enhancement of CNT dispersion by using the solvent similar to other reports [Liao et al., 2004; Park et al., 2003; Barrau et al., 2005; Yuen et al., 2007] was revealed by infrared optical microscopy and SEM analyses. The SEM images showed that the unidirectional cleavage and smooth fracture surfaces of the neat epoxy matrices became isotropic and rough after the introduction of the fillers for both the series. However, the MWCNT aggregates (series 1) were concentrated in small areas whereas in composites (series 2), the nanotube bundle distribution seems more homogeneous throughout the entire surface.

2.1.2 Thermal and mechanical properties

Composite materials consisting of a polymer and CNTs frequently exhibit improved thermal and mechanical properties when compared to those of pristine polymers containing a small amount of CNTs. Improvements include higher modulus, increased strength, thermal and thermo-mechanical stability. However, the degree of improvement of thermal and mechanical properties of expoxy-based composites materials directly depends on the nature of MWCNTs and matrix, and also the method used to fabricate composites.

Schadler et al. [Schadler et al., 1998] studied the mechanical behaviour of the epoxy composite with CVD-grown CNTs under compression and tension by measuring the shift for the sensitive second order CNT-Raman peak at 2700 cm⁻¹[Rao et al., 1997]. The analysis showed a larger Raman peak shift in compression (7 cm⁻¹ negative) compared to tension,

showing effective load transfer. The composite modulus increased significantly in compression mode with respect to pure resin. The similar types of results also reported by Cooper et al. [Cooper et al., 2001] by observing the stress-induced Raman shift, the modulus of MWCNT composite was calculated as 0.3 TPa.

Table 5 shows the effect of surfactant on the thermo-mechanical properties of CNT-epoxy composites [Gong et al., 2000]. From the results it is obvious that while the addition of CNTs alone increases the storage modulus and glass transition temperature (T_g) moderately (surfactant by itself has little effect), both properties increase significantly with the addition of CNTs in the presence of the surfactant. Addition of 1 wt% CNTs gave more than 30% improvement in storage modulus.

On the other hand, Cui and co-workers [Cui et al., 2003] found that a higher amount of the surfactant decreased T_g because of the plasticizer effect, although MWCNTs were homogeneously dispersed in the epoxy matrix. A regular increase of T_g with tube content was observed for the samples without surfactant, which could be associated with increasing interface area with a rather good anchoring [Keddie et al., 1994; Long et al., 2001]. There was no significant change of T_g with the series prepared with surfactant, which contradicts the results from Gong et al. [Gong et al., 2000]

Samples		G' (GPa)		$T_{\rm g}$ (°C)
	-60 (°C)	-20 (°C)	20 (°C)	tanδ	G″
(a) epoxy	1.90	1.65	1.43	63	50
(b) $epoxy + C_{12} EO_8$	1.53	1.38	1.20	62	47
(c) epoxy + 1 % tube	2.12	1.90	1.60	72	53
(d) $epoxy + C_{12} EO_8 + 1\%$ tube	2.54	2.18	1.80	88	64

Table 5. Storage moduli and glass transition temperatures (T_g) of pure epoxy and composite samples. Reproduced from Gong et al.,2000.

The hardness and flexural properties of epoxy composite containing varying amount of CNTs were studied by Lau and colleagues [Lau et al., 2003]. The hardness of the CNT-composites was superior to that the pure epoxy and the hardness increased with CNT content. However, the bending strength of pure epoxy decreased with the introduction of CNTs, revealing that the load was not transferred effectively to the CNTs due to poor interfacial interaction. Park et al. [Park et al., 2003] also used sonication to prepare the composites. The tensile strength and modulus of composite increased with increase in CNT content (0.5 to 2 vol%), whereas elongation at break decreased systematically. A 50% improvement in tensile strength was observed with 2 vol% of CNTs, and the modulus increased two times compared to the pure resin.

Wan et al. measured the mechanical properties of CNT-epoxy thin film prepared by spin coating using a shaft-loaded blister method [Wan et al., 1999]. The results showed that 0.1 wt% of CNTs loading can enhance the elastic modulus of the pure epoxy thin film by 20%, however, the failure strain of composite was lower than neat resin. This is due to strong interfacial bonding between CNTs and the matrix.

The effect of oxyfluorination of CNTs on the surface fracture properties of epoxy matrix was also reported [Park et al., 2004]. Impact strength and fracture toughness showed maximum values for the composite prepared using CNTs with highest surface oxygen and fluorine groups. Oxyfluorination contributed to the enhancement of adhesive forces between the filler and epoxy by changing the surface polarity and activity of CNTs.

In another report, Xie et al. [Xie et al., 2000] analysed the cure kinetics of an industrially used epoxy polymer TGDDM/DDS blended with MWCNTs using differential scanning calorimetry (DSC). Previous studies showed autocatalytic mechanism for TGDDM/DDS composite curing [Cole et al., 1991; Nam et al., 1993; Barral et al., 1998]. The present study revealed the accelerating effect of MWCNTs on the epoxy curing reaction during the initial stage (autocatalytic nature), which decreased with increasing amounts of CNTs. The catalytic effect of MWCNTs in the initial stage was attributed to the surface –OH groups which help in opening the epoxide rings. The reaction becomes diffusion controlled at higher CNT content. The authors used the autocatalytic model by Sourour and Kamal [Sourour & Kamal, 1976] with modification through diffusion control function to explain the entire curing process.



Fig. 17. The effect of MWCNTs and MWCNTs-NH₂ content on: (a) impact strength and (b) bending modulus of MWCNTs-containing epoxy composites. Reproduced from Yaping et al., 2006.

Compound	Structure
Ethylenediamine (e-MWCNT)	H ₂ NH ₂ CCH ₂ NH ₂
1,6-Hexanediamine (h-MWCNT)	$H_2NH_2CCH_2CH_2CH_2CH_2NH_2$
4,4'- Diaminodiphenylmethane (p-MWCNT)	H ₂ NCH ₂ NH ₂
4,4'-Diamino-dicyclohexyl methane (c-MWCNT)	H ₂ N — CH ₂ — NH ₂

Table 6. Exact compounds for different functionalization. Reproduced from Shen et al., 2007

Epoxy composites prepared with amine functionalized MWCNTs were used to investigate the thermo-mechanical properties [Gojny et al., 2004]. The results from dynamic-mechanical thermal analysis (DMTA) showed a strong increase in storage modulus around T_g below which there was no noticeable effect. The loss modulus also increased from 0.05 wt% CNTs

but decreased at higher CNT-content probably due to agglomeration. The addition of CNTs (nonfunctionalized and amine-functionalized) showed distinctive increase in $T_{\rm g}$ for the composites. Stronger increase in Tg was observed for amine-functionalized CNTs with linear dependence on CNT-content. Yaping et al. [Yaping et al., 2006] used multi-functional amine (DETA) for the functionalization of CNTs before adding them to epoxy matrix. They also found that with amine functionalization the CNTs can be better dispersed in the matrix, leading to enhancement in mechanical properties (refer Fig. 17). A significant increase in bending strength and flexural modulus (100% and 58%) could be obtained with very small amount of CNTs (0.6 wt%). Shen et al. [Shen et al., 2007] investigated the reinforcing role of different amine-functionalized MWCNTs in epoxy composites. The thermal decomposition temperature for all the amine-modified CNT-epoxy was higher than that of the pure resin. A maximum increase of 35°C was observed for 0.25 wt% p-MWCNTs (pure MWCNTs) whereas h-MWCNTs (amine functionalized MWCNTs) had the least effect (refer Table 6). Higher amounts of CNTs decreased the decomposition temperature. Introduction of CNTs to the matrix increased the flexural strength and modulus where p-MWCNTs gave the best results. However, they observed a decrease in T_g with amine-functionalized CNTs. Barrau et al. [Barrau et al., 2005] also reported T_g depression of 5°C for the epoxy composite when the CNT content was in the range 0-0.04 wt%. The glassy storage modulus increased below $T_{\rm g}$ with the addition of the filler though the increase was not linear over the CNT range.

The increase in T_g with the addition of MWCNTs was also reported by Ganguli et al. [Ganguli et al., 2005] MWCNTs significantly increased the ultimate strength and strain to failure of epoxy resin. In comparison to OLS fillers (17% increase), CNTs showed increased fracture toughness (170% increase) when mixed with neat epoxy.

The stiffness and damping properties of the CNT-epoxy composite were examined by Rajoria et al. [Rajoria et al., 2005] with free and forced vibration tests. A 700% increase in damping ratio was observed with an optimum 5 wt% CNTs. Though storage modulus was not affected by CNT addition, loss modulus increased with CNT content and showed a maximum at 7.5 wt%. The stick and slip mechanism was used to explain the increase in damping ratio with no change in stiffness, which implies poor adhesion with no significant load transfer between the filler and epoxy.

Liu et al. [Liu et al., 2005] compared the effect of amine-functionalized CNT rubbery (Epon 828/D-2000) and glassy (Epon 828/ T-403) epoxy polymers. With 1 wt% of CNTs, the rubbery matrix showed significant improvement in tensile modulus (28%), tensile strength and breaking strain, whereas the glassy matrix showed no marginal increase in properties except for the impact toughness. From these observations it is clear that low viscosity epoxy matrix is advantageous for CNT fillers in composite processing. The reinforcing effect of MWCNTs in two different epoxy polymers (Epon 815 and LY 564) has been investigated by Fidelus et al. [Fidelus et al., 2005]. The nanotubes were dispersed using SDS as the surfactant. A large reduction in $T_{\rm g}$ was observed for LY 564 with 0.5 wt% of CNTs. By contrast Epon 815 showed no change. A moderate increase in Young's modulus was observed for all the composites. LY 564 showed substantial improvement in the tensile strength (70% with 0.5 wt% and 50% with 0.05 wt% MWCNTs loading) while for Epon 815 there was no noticeable change. The reinforcing effect of CNTs was found to be different for different polymer matrices. Ci et al. [Ci et al., 2006] prepared epoxy matrices with different stiffness by controlling the curing step and investigated the reinforcing effect of MWCNTs. According to the results, CNTs have a more significant role in the soft matrix than in the hard matrix. 0.5 wt% of CNTs was found to be enough to produce a 200% increase in Young's modulus and up to 140% increase in tensile strength, and these values decreased with increasing hardness of the matrix. Camponeschi et al. [Caponeschi et al., 2007] examined the alignment effect of MWCNTs under magnetic field on the mechanical properties of two different epoxy matrices. The AP system showed an increase in tensile modulus and Young's modulus when compared to the coldfix system. When compared to the pure epoxy, the CF-based system showed a detrimental effect on all the properties. The results showed that the alignment of CNTs under magnetic field that leads to improvement in properties depends on the polymer matrices.

The influence of MWCNTs on the friction and wear behaviours of epoxy composites was studied by Dong et al. [Dong et al., 2005] and results are summarized in Fig. 18. The increase in microhardness and reduction in friction coefficient were optimum at 1. 5 wt% of MWCNTs. The composite showed lower wear rate compared to pure epoxy polymer. The mechanical reinforcing and self-lubricating properties of MWCNTs help to improve the tribological behaviors of the composite. Zhang et al. [Zhang et al., 2006] also reported the wear properties of CNT-epoxy composites prepared by the ultrasonication method. Addition of only 0.1 wt% of CNTs dramatically reduced the wear rate when compared to the pure epoxy matrix. However, the contact sliding in the wear test is reported to deform the CNTs leading to its fragmentation. Chen et al. [Chen et al., 2007] proposed sonication as a better CNT dispersion method to decrease wear rate for the composites.



Fig. 18. Variation of the (a) microhardness and (b) friction coefficient of MWCNTs-epoxy composites with MWCNTs content. Reproduced from Dong et al., 2005.

Ganguli et al. [Ganguli et al., 2006] in another work used MWCNTs surface modified by different methods to reinforce the epoxy matrix. About 10% increase in the onset point of thermal degradation and a 30-40% decrease in the coefficient of thermal expansion (CTE) were observed for all the nanocomposites. Ball-milled and acid-treated samples exhibited better mechanical properties with 0.1 wt% CNTs. 0.15 wt% gave better results where the fracture toughness increased by 40% and 80%, respectively for ball-milled and acid-treated MWCNTs dispersed in epoxy to fabricate composites with glass fibre by the VARTM method. With 1 wt% loading of acid-treated MWCNTs, noticeable enhancement in tensile strength, Young's modulus (14% and 20% respectively) and toughness were observed. They also reported a decrease in CTE (25.2%) with the introduction of CNTs to the polymer matrix. Bekyarova et al. [Bekyarova et al., 2007] also used the VARTM technique to produce a CNT-carbon fibre-

Fillers	Tensile strength (MPa)	Young's modulus (GPa)	Elongation at break (%)
No filler (epoxy)	26	1.21	2.33
Untreated CNTs	42	1.38	3.83
Acid treated CNTs	44	1.22	4.94
Amine treated CNTs	47	1.23	4.72
Plasma treated CNTs	58	1.61	5.22

epoxy composite. The addition of 0.25% of CNTs resulted in an enhancement of interlaminar shear strength by 27%. Santos et al. [Santos et al., 2008] reported no change in CTE for composites prepared with CNTs dispersed with the help of SDS and acetone.

Table 7. Mechanical properties of pure epoxy and CNT-epoxy composites . Reproduced from Kim et al., 2006.

The mechanical properties of composites prepared using MWCNTs functionalized through different methods are summarized in Table 7 [Kim et al., 2006]. Tensile strength, elongation at break and Young's modulus of the surface modified CNT-epoxy composite were higher when compared to the neat resin. The results were very good, with plasma-treated CNT sample showing the effectiveness of this surface modification. Tseng et al., [Tseng et al., 2007] functionalized MWCNTs by plasma treatment followed MA grafting and prepared a CNT-epoxy composite. Just 0-1 wt% CNTs produced elongation upto 43% (380% increased as compared to the pristine epoxy) and more than 100% improvement in tensile modulus. The Tg also increased significantly with the addition of CNTs (increase was greater for MA-CNTs-epoxy system). Chen and colleagues [Chen et al., 2006] tried two-step acid epoxy functionalization of MWCNTs to improve the dispersibility and flexural strength of the composite. Functionalization with two different epoxides polyethylene glycol (PEG) and DGEBA led to stable and uniform dispersion of CNTs in epoxy. PEG functionalization (monoepoxide) was more efficient in enhancing flexural strength and elastic modulus of the composite. The higher efficiency of PEG was attributed to the presence of more surfaces -OH groups on MWCNTs available for chemical bond formation with epoxy matrix. Abdalla and co-workers [Abdalla et al., 2007] used carboxylated and fluorinated CNTs to reinforce the epoxy matrix. Both functionalizations showed positive results on the mechanical properties, though fluorinated CNTs showed the highest values. T_g and shear moduli were higher for the composites with 1 wt% CNTs.

Thostenson and co-workers [Thostenson et al., 2006] studied the effect of processing conditions on the mechanical properties of composites prepared through intense shear mixing by the calendering method. Though the CNTs were more dispersed with a processing gap setting of 5 μ m, the fracture toughness was higher for composites processed at 10 μ m. The thermal conductivity showed a linear relationship with CNT content; with the highest concentration of 5 wt%, about 60% increase in thermal conductivity was measured. Increase in thermal conductivity with CNT-content was also reported by Moisala et al. [Moisala et al., 2006] On the other hand; Yuen et al. [Yuen et al., 2007] reported no significant improvement in thermal conductivity by adding CNTs to the epoxy matrix, though $T_{\rm g}$ increased rapidly when the CNT content was below 0.1 wt%. Chen et al. [Chen et al., 2007] tried different CNT treatments and mixing methods to prepare CNT-epoxy matrices and investigated the thermo-mechanical properties. The results indicated that only in the absence of effective dispersion methods like speed mixing or sonication, is pre-

treatment of CNTs (with acid or coupling agent) necessary. The sample produced by the combination of sonication and speed mixing (untreated) showed the highest values for storage modulus and T_{g} , and the values were very close to those prepared using pre-treated CNTs. Sonication was found to be disadvantageous for acid-treated CNTs as it leads to fracture of pre-damaged CNTs.

While analysing the effect of CNT content and curing temperature on the flexural properties of epoxy matrix, Zhuang et al. [Zhuang et al., 2006] found that the composites possess higher strength at MWCNT content in the range of 0.05–0.1 wt%. A maximum of 9% increase with respect to pure epoxy was observed with 0.075 wt% CNTs. Composites with the same CNT content cured at different temperatures indicated a reinforcing effect between 100 and 120°C. The stiffening effect disappeared at higher temperatures.

An instrumented indentation technique to measure the elastic modulus and hardness of CNT array-epoxy composites was employed by Lee et al. [Lee et al., 2007]. A steady increase in elastic modulus of the composite up to 75% was observed when compared to the neat resin over the entire range of indentation test.

On the other hand, Zhou and co-workers showed that during processing, there is a strong effect of sonication intensity on the thermal and mechanical properties of CNT-epoxy composites [Zhou et al., 2003]. Studies revealed a steady increase in storage modulus with CNT content (93% with 0.4 wt% of CNTs) and about 22°C increase in T_g . However, the decomposition temperature of the composite decreased for composites with higher amounts of CNTs. The modulus also showed gradual increase (11.7% with 0.4 wt% CNTs), but the tensile strength reached a maximum at 0.3 wt% filler content (28.3% improvement). However, Sandoval et al. [Sandoval et al., 2007] used non-localized ultrasonic dispersion to introduce MWCNTs to epoxy matrix. CNTs at a concentration of 0.05% (w/v) in WaterShedTM resulted in an increase of the ultimate tensile strength, fracture strength and hardness at temperatures beyond ~200°C. A 51.8% increase in Young's modulus was noticed with the introduction of 5 wt% CNTs when compared to the pure epoxy specimen [153]. Composites were prepared by hot press. The tensile strength showed a 17.5% increase with 3 wt% of MWCNTs. The properties decreased at higher amount of CNTs.



Fig. 19. DMA results of neat epoxy, CSD/epoxy, and CMW/epoxy composites: (a) storage modulus (E') and (b) loss factor (tan δ). Reproduced from Perez et al., 2008

Garcia and co-workers [García et al., 2007] used dimensions measured from SEM images to predict the Young's modulus of a vertically aligned (VA) CNT array-epoxy composite. The Young's modulus increased from 3.7 to 12 GPa, and the reinforcement for the CNT pillars was 220%, showing effective reinforcement. On the other hand, Yaglioglu et al. [Yaglioglu et al., 2008] proposed a novel technique to transfer VA-CNTs to copper substrate using epoxy polymer. The Young's modulus of CNT-epoxy composite pillars was calculated to be 1.2 GPa when compared to the as-grown CNT columns (2.2 MPa).

Pèrez and co-workers [Pèrez et al., 2008] investigated the effect of aspect ratio of MWCNTs on the mechanical properties of the epoxy system. The introduction of nanotubes (CSD or CMW) made the epoxy resin slightly more flexible and tougher with no noticeable increase in strength and a decrease in elastic modulus. These properties were similar for different types of CNTs. However, the impact strength of the epoxy resin improved by 84% when 1 wt% of higher aspect ratio tubes (CMW) were mixed with the resin, and by 63% when the same amount of CSD tubes were used. The storage modulus of CSD epoxy, which was lower than that of neat resin below 97°C, increased between 97 and 135°C. For CMW composites storage modulus was much higher. Both the composites showed an increase in T_g values (refer Fig. 19). Li and co-workers [Li et al., 2008] used a CNT/GNP hybrid to reinforce epoxy matrix. The flexural modulus of the composite was 21% higher than that of the pure epoxy matrix while the flexural strength was not affected. The fracture toughness showed 21% improvement compared to 2 wt% GNP alone and 57% compared to neat epoxy.

2.1.3 Electrical properties

Over the last few years, the potential use MWCNTs as conducting fillers to improve the electrical conductivity of epoxy matrix has been established. Several authors have reported significant enhancement in electrical conductivity with a very small loading of MWCNTs in the epoxy matrix, while maintaining the mechanical performance of composites. Sandler et al. [Sandler et al., 1999] reported the electrical conductivity of an epoxy matrix containing untreated CNTs around 10⁻² Sm⁻¹ at a filler content of 0.1 vol% which is much higher compared to the composite containing conventional carbon black filler. The conductivity showed gradual increase with CNT content. The percolation threshold was found to be in between 0.0225 and 0.04 vol% of CNTs. Park et al. [Park et al., 2003] also found that the resistivity of composite decreased with CNT content, and the threshold concentration reached 0.5 vol.% of CNTs. However, Cui et al. [Cui et al., 2003] reported a relatively high percolation threshold around 8 wt% of CNTs for two series of epoxy composites prepared with and without surfactant from D.C. resistivity measurements. The wrapping of the CNT surface by the surfactant prevents particle-particle interaction and contributes to the high critical wt% of the filler to attain percolation network.

On the other hand, Sandler and co-workers [Sandler et al., 2003] suggested the used of aligned MWCNTs to get a uniquely low percolation threshold. CNT concentration of about 0.0025 wt% was found to be enough to produce the conducting network within the epoxy matrix in this case. Martin et al. [Martin et al., 2004] reported similar results in another work. The bulk conductivity values varied from dielectric nature to 10⁻³ depending on the nanotube aggregation and dispersion levels obtained under various processing conditions. According to them, the processing parameters should be carefully adjusted to achieve very low percolation threshold. Moisala et al. [Moisala et al., 2006] also prepared conductive epoxy composite with MWCNTs with a percolation threshold of 0.0025 wt% using high shear mixing procedure proposed by Sandler et al. [Sandler et al., 2003]. Li and co-workers [Li et al.,

2007] investigated the electrical properties of composites prepared using four different processing conditions. The D.C. conductivity was different for different composites. The results suggested that the formation of conductive CNT network requires a moderate aspect ratio of CNTs and this phenomenon is independent of CNT dispersion state.

Martin et al. [Martin et al., 2005] in another work used A.C. and D.C. electric fields to align a conductive CNT network in epoxy matrix. The network formed under the A.C. field was more uniform and aligned in comparison to that formed under the D.C. field, and hence, the maximum current density was higher for composite formed in the A.C. field. Increase in current density was observed in both the cases with CNT content (0.005–0.02 wt%).

In a very interesting work, Thostenson and co-workers [Thostenson et al., 2006] prepared composites using the calendering approach and optimized the processing conditions. As seen in Fig. 20, composite with higher CNT dispersion obtained with a 5 μ m gap setting showed lower electrical resistivity than that with agglomerated structure especially at lower CNT-content. The effect of processing conditions on electrical conductivity was also investigated by Hu et al. [Hu et al., 2008]. Electrical conductivity of various samples are presented in Fig. 21. It can be seen from figure that the conductivity of the samples prepared with the solvent (B and C) are lower than that of A (without solvent). Higher curing temperature is found to be effective (C) in establishing conducting network in the matrix. The lower conductivity value for sample E revealed that long mixing time has a detrimental effect on conductivity. The procedure in which CNTs were added to the pre-prepared epoxy/hardener increased the conductivity (E). Comparison of samples G and H indicated that slower mixing speed increased the conductivity significantly (see Table 4 for the fabrication conditions).



Fig. 20. DC volume resistivity of the as-processed composites showing percolation thresholds occurring below 0.1%. Reproduced from Thostenson et al., 2006.



Fig. 21. Electrical conductivities of various samples (note that the electrical conductivity of Sample B is lower than 10^{-6} S/m). Reproduced from Hu et al., 2008.



Fig. 22. Comparative plot of the ac conductivity of the CNT-epoxy nanocomposite as a function of the CNT content. Reproduced from Tseng et al., 2007.

The A.C. conductivity of epoxy composite containing plasma-treated MA-modified CNTs was measured by Tseng et al. [Teseng et al., 2007] and corresponding values are presented in Fig. 22. The results showed an increase in conductivity with the introduction of CNTs to the epoxy system, which improved with CNT content. However, the epoxy with

functionalized CNTs showed a lower percolation threshold (0.1–0.2 wt%) than the one with untreated CNTs (0.5–0.6 wt%). Improved conductivity could be attributed to better dispersion of CNTs, which lowers the amount of CNTs required for the formation of conductive network, which contradicts the results by Li et al [Li et al., 2007].

Bekyarova et al. [Bekyarova et al., 2007] demonstrated the enhancement of out-of-plane conductivity by depositing a small amount of MWCNTs on CF and using it as filler in epoxy matrix. A remarkable increase in electrical conductivity by using CNT/GNP filler in epoxy was demonstrated by Li et al. [Li et al., 2008]. Sandoval et al. [Sandoval et al., 2007] also reported a decrease in electrical resistivity in CNT-epoxy composite with percolation threshold around 0.6 wt%. Sandos and co-workers [Sandos et al., 2008] proposed 0.5 wt% of CNTs as the critical concentration to get improved electrical conductivity for the CNT-epoxy composite prepared by using a surfactant and acetone solvent.



Fig. 23. Comparative plot of the composite conductivity as a function of nanotube weight fraction for the three different sample preparation methods. Reproduced from Kovacs et al., 2007.

On the other hand, for the first time, the possibility of the co-existence of two percolation thresholds was proposed by Kovacs et al. [Kovacs et al., 2007]. Fig. 23 shows the comparative plot of the composite conductivity as a function of nanotube weight fraction for the three different sample prepared using three different methods. Results showed that the percolation concentrations of 0.011, 0.024 and 0.08 wt% for composites prepared by slow, medium and fast stirring, respectively, in the kinetic region (below 0.1 wt% CNT content) due to the emergence of networks between dispersed immobile CNT particles. A plateau was observed thereafter in all the cases similar to that reported by Sandler et al. [Sandler et al., 2003], where the flocculation cannot further improve conductivity through the network. As the concentration increases above 0.1 wt% additional conducting channels establish increasing conductivity.

Pèrez and co-workers [Pèrez et al., 2008] used MWCNTs of different aspect ratios (CSD and CMW) in the epoxy matrix and studied the electrical properties of the resulting composites.

Measurement of D.C. electrical conductivity indicated that introduction of CSD CNTs has no effect on the conductivity of the epoxy matrix, whereas the high aspect ratio CMW CNTs increased the conductivity of pure resin by 10 orders of magnitude. The percolation threshold was found to be 1 wt% for these composites.

2.2 SWCNT containing epoxy composites

SWCNTs consist of a single sheet of graphene rolled seamlessy to form a cylinder with diameter of order of 1 nm and length up to centimetres. Some SWCNTs are stronger than steel, lighter than aluminium, and more conductive than copper. For example, theoretical and experimental results on individual SWCNTs show extremely high tensile modulus (640 GPa to 1 TPa) and tensile strength (150-180 GPa). Not only that depending on their structural parameters, SWCNT can be metallic or semiconducting. Because of these extraordinary properties of single SWCNT, there is a great enthusiasm to incorporate SWCNTs into the epoxy matrix to fabricate electrically conductive materials with balance of mechanical properties. Over the last few years, researchers are using different techniques to disperse SWCNTs in epoxy matrix. The section below reviewes the preparation and physicochemical characterization of various types SWCNTs-containing epoxy composites.

2.2.1 Preparative methods and morphological study

In 2001, Cooper et al. [Cooper et al., 2001] first used SWCNTs as reinforcement for epoxy polymer matrix. The used SWCNTs were synthesized by two different methods such as pulsed-laser SWCNT-P and arc-discharge SWCNT-A. The composites were fabricated by the same procedure used for the preparation of MWCNTs-containing epoxy composites (see section 2.1.1). Ultrasonication was used to incorporate SWCNTs into epoxy resin by Puglia and co-workers [Puglia et al., 2003 a; Puglia et al., 2003 b]. 5 and 10 wt% of SWCNTs (diameter 1.2-2 nm, length several µm) were ultrasonically dispersed for 2 h in the liquid epoxy resin (DGEBA). All samples were then cured with DETA hardener (DETA/DGEBA = 1:7.25) using a cure schedule with a temperature ramp from 30 to 150°C at a heating rate of 10°C/min. The SEM images of the composite with 5 wt% SWCNTs loading showed good interaction between the filler and the epoxy matrix that helps in opening CNT bundles and dispersing the tubes. The same technique was also used by Barrau et al. [Barrau et al., 2003b] for the synthesis of CNT-composite with bisphenol-A epoxy polymer (LY5641) and an amine hardener (HY2954 at resin/curing agent ratio 100/35) by sonication. Purified SWCNTs synthesized by the CVD method (0.04 to 2.5 wt%) were dispersed in ethanol using ultrasonication at RT for 2 h. The liquid epoxy resin was added to the dilute suspension of nanotubes, and the mixture was again sonicated for 1 h. The solvent was removed in a vacuum oven at 80°C, and the mixture was stirred at 2000 rpm for 1 h. The hardener was then added and mixed mechanically at 2000 rpm for 15 min. The mixture was molded and then returned to vacuum for 20 min for degassing. The epoxy matrix was cured in the oven at 120°C for 20 min and then at 145°C for 4 h.

In another work, Barrau et al. [Barrau et al., 2003 a] used palmitic acid $(C_{16}H_{32}O_2)$ as a surfactant for the dispersion of CNTs in epoxy polymer solution used in the previous study [Barrau et al., 2003 b]. Acid-purified SWCNTs (content varied between 0.05 and 0.8 wt%) were not dried after acid purification to prevent their agglomeration in bundles. Epoxy resin was added to the CNT solution in water, and the mixture was sonicated for 1 h and dried in a vacuum oven at 100°C for 1. Palmitic acid was then added, and the mixture was sonicated

for 1 h at RT. The ratio of nanotubes to palmitic acid varied from 1:2 to 2:1 by weight. Hardener was added subsequently and mechanically mixed. The final mixture was moulded and cured in an oven at 120°C for 20 min and 145°C for 4 h. The SEM images of composite fractured surfaces are given in Fig. 24. The SEM images showed good dispersion of CNTs in the samples prepared with the surfactant. Individual CNTs covered with the surfactant were homogeneously dispersed in the matrix.



Fig. 24. Field emission SEM images of: (a) CNT-C16H32O2- epoxy composite for 0.8 wt % CNTs and 1:1 CNTs to $C_{16}H_{32}O_2$ weight ratio. The arrows indicate (A) individual CNTs and (B) CNTs covered with palmitic acid. (b) CNT-epoxy composite for 0.8 wt % CNTs without palmitic acid. The scale bar corresponds to 200 nm. Reproduced from Barrau et al., 2003a.

Significant improvement in the dispersion of SWCNTs was obtained by Zhu and co-workers [Zhu et al., 2003] through acid treatment and subsequent fluorination. HiPco produced SWCNTs were sonicated for 1 h in a 3:1 mixture of H_2SO_4/HNO_3 (70%), washed with NaOH and dried at 70°C overnight. Acid-treated nanotubes were fluorinated [Mickelson et al., 1998] in a Monel reactor heated to 150°C for 12 h with a gas-flow ratio for F₂ and He was 1:10 The functionalized nanotubes (F-SWCNTs) were dispersed in DMF (2 mg/mL) by sonication for 5 min and then for 1 h in an ultrasonic bath. The epoxy resin (Epon 862) was then added, and the solution was stirred for 30 min. DMF was evaporated at 100°C in a vacuum chamber, and the blend was stirred for 5 min with a high-shear mixer. Further stirring was done after adding the curing agent, Epicure W. The blend was degassed for 5 h in a vacuum oven, moulded and cured at 100°C under a pressure of 0.3 MPa for 2 h followed by another cycle of 2 h at 160°C. Optical micrographs and SEM images revealed noticeable enhancement in dispersion of F-SWCNTs throughout the epoxy matrix in comparison with that of the pristine SWCNTs.

Ren and co-workers [Ren et al., 2003] used aligned SWCNTs produced by the arc-discharge [Liu et al., 2000] method for the preparation of reinforced epoxy composite. To fabricate the composite sample, a thin layer of epoxy resin (Epicote 1006) was evenly brushed onto a hard surface. 20 mm-long SWCNT ropes (0.1–0.9 vol.%) were then aligned by a slight tension and laid onto the epoxy layer. More epoxy was then applied to cover the SWCNT ropes, and the composite was cured for 72 h at RT. The SEM image of the fatigue fracture surface, showed good wetting of CNT ropes in epoxy, which indicated strong interfacial adhesion. The long pull out length of CNTs suggested high shear stress between the phases.

In another work, Gou et al. [Gou et al., 2004] fabricated epoxy composites with HiPco bucky paper containing SWCNTs. Epon 862 epoxy resin and Epicure W curing agent were mixed at a weight ratio of 100:26.4 and diluted with acetone. The composite was prepared by the infiltration of resin solution through the bucky paper followed by hot pressing. The sample was cured for 2.5 h at 177°C under pressure, cooled to RT, post-cured at 177°C for 2 h and finally, cooled to RT inside the oven. The SEM analysis showed the presence of curved and interwoven SWCNTs on the composite surface indicating good wetting between the CNTs and epoxy.

The arc discharge-produced SWCNTs were also used for reinforcing epoxy polymer [Valentini et al., 2004]. SWCNTs were purified by selective oxidation and acid refluxing followed by vacuum annealing. SWCNTs (5 and 10 wt%) were sonically dispersed for 2 h in the liquid epoxy resin (DGEBA). All samples were then cured after adding DETA hardener (DETA: DGEBA 1:7.25) with a temperature ramp from 30 to 150°C at a heating rate of 10°C/min. SWCNT-epoxy composites were prepared using an ultrasonication procedure by Zhou et al. [Zhu et al., 2004].

Sample no.	Tip sonication (h)	Bath sonication (h)	Surfactant	Acetone
1	0	0	Yes	Yes
2	6	6	0	0
3	6	0	0	Yes
4	0	6	Yes	0
5	6	0	Yes	0
6	6	6	Yes	Yes

Table 8. Processing parameters of nanocomposite samples. Reproduced from Liao et al., 2004.

Liao et al. [Liao et al., 2004] investigated the various dispersion processes of SWCNT in SC-15 epoxy matrix. BYK-9076 surfactant was added into SC-15 resin solution in acetone. SWCNTs (0.5 wt%) were added to this solution and manually stirred for 10 min. Tip and bath sonication were used to further disperse the nanotubes. The mixture was vacuum dried



Fig. 25. SEM images of (a) SC-15 neat resin, (b) and (c) nanocomposite (sample 3). Reproduced from Liao et al., 2004

at 75°C for 1 h and then cooled to RT. Finally, the mixture was molded and cured in an oven at 60°C for 2 h followed by post-curing at 93.3°C for another 4 h. The composite processing conditions are given in Table 8. The neat resin showed a smooth surface which can propagate cracks easily in the SEM images [see Fig. 25 (a)]. However, the higher degree of surface roughness with highly curved crack propagation pattern was observed for the nanocomposite [see Fig. 25 (b)].

To study the effect of incorporation of SWCNTs on the nanomechanical properties of epoxy matrix, Li and co-workers [Li et al., 2004] prepared a series of composites with varying SWCNTs loading. In a typical procedure, Epoxy monomer [1,1-bis (4-cyanatophenyl) ethane] pre-polymerized at 80°C for 48 h was also dissolved in THF. 2 g of SWCNTs were purified by acid refluxing, functionalized with methyl-4-aminobenzoate [Bahr et al., 2001, Dyke et al., 2003], dispersed in THF and added to the pre-polymer solution. After removing the solvent, the composite was dried in a vacuum oven at 60°C for 12 h. The final mixture was then molded and cured at 170°C for 12 h. Investigations on the surface morphology of the composite by SEM indicated better dispersion of tubes at lower concentration. Wrapping of tubes with the polymer showed good adhesion between the two components. However, at higher CNT content, CNT agglomerates were found.

On the other hand, Wang et al. [Wang et al., 2004] used the infiltration method as reported by Gou et al. [Gou et al., 2004] to fabricate SWCNT-reinforced epoxy composites. The SWCNTs (diameter 0.8-1.2 nm, length 10-1000 nm) were first dispersed into water with the aid of Triton X-100 surfactant and then sonicated to form a well-dispersed and stable suspension. The SWCNTs suspension was filtrated to form buckypapers which were composed of uniform SWCNT rope networks. The low viscosity resin solution (Epon 862 and the curing agent was Epicure W mixed at a weight ratio of 100:26.4) was allowed to infiltrate the buckypapers to impregnate the SWCNT rope networks. The composites (up to 39 wt%) were moulded in a hot press and cured at 177°C for 2.5 h under pressure, cooled to RT and post-cured in the oven for another 2 h. The AFM and SEM examinations of the composite fracture surface revealed uniform impregnation of epoxy throughout the buckypaper. In another publication Lucas et al. [Lucas et al., 2004] used SWCNTs from HiPco method [Nikolaev et al., 1999] to disperse in Araldite epoxy resin LY5052. Fluorinated SWCNTs (FSWCNTs) were employed by Miyagawa et al. [Miyagawa et al., 2004] to improve the properties of epoxy polymer. Use of FSWCNTs was previously reported by Zhu et al. [Zhu et al., 2003]. FSWCNTs (up to 0.5 wt%) were sonicated in acetone for more than 5 h (1 g/1000 ml). Epon 862 epoxy resin was processed with curing agent methyltetrahydrophthalic-anhydride (MTHPA), aradure HY 917 and an accelerator 1methylimidazole DY 070 at the ratio 100:92.7:1 and added to the FSWCNT solution under magnetic stirring for 1 h. The acetone was removed by vacuum extraction at approximately 100°C for 24 h, and then MTHPA and 1-methylimidazole were blended into the solution. The specimens were cured at 80°C for 4 h followed by 160°C for 2 h. In a subsequent work, the same group synthesized composites using FSWCNTs and bio-based epoxy polymer [a mixture of Epon 862 and epoxidized linseed oil (ELO)] following the same procedure [Miyagawa et al., 2005].

Yun et al. [Yun et al., 2005] demonstrated a simple method for the fabrication of a novel SWCNT-epoxy composite material. The purified SWCNTs were dispersed in DMF by mixing for 5 h and low level ultrasonication for 2 h. This solution was molded and dried at

180°C for 5 h under vacuum to produce a nanotube paper. Epoxy (Epon 862) and a curing agent (Epicure W) were mixed well without any solvent and then applied on the surface of the nanotube paper. This layered composite was cured in an oven for 4 h at 120°C.

Brown et al. [Brown et al., 2005] obtained improved dispersion of HiPco synthesized SWCNTs in an epoxy matrix by the sonication method. In a typical synthetic method, 0.01 g SWCNTs were first purified [Strong et al., 2003] and added to 7.25 g of Jeffamine D2000 (curing agent), and the mixture was sonicated for 3 min. 2.75 g of Epon 828 heated at 75°C was added to the SWCNTs/D2000 mixture. One formulation was made with conventional mixing with epoxy. Other formulations were sonicated for 1 h at 75°C after adding the epoxy. The samples were molded and cured for 2 h at 75°C followed by 2 h at 125°C. SEM analysis showed good wetting of highly dispersed CNTs by epoxy without any CNT pull out. The TEM image revealed a well distributed network of SWCNTs on rheological, mechanical and thermal properties of epoxy composites, Song et al. [Song et al., 2005] prepared a series of SWCNTs-containg epoxy composites.

The solvent effect for SWCNTs dispersion was also demonstrated by Lau and co-workers [Lau et al., 2005] SWCNTs (0.5 wt%) were dispersed into one of the solvents (acetone, ethanol or DMF) with strong sonication for 1 h. Epoxy resin (Araldite GY 251) was added into the CNT suspension and sonicated for another hour. The mixture was then placed on a hot plate at 60, 80 and 140°C for 45, 70 and 110 min for acetone, ethanol and DMF, respectively, to completely evaporate the solvent. All the samples were degassed for 4 h, molded and cured after the amine hardener (CIBA HY 956) was added. The samples were pre-cured on a hot plate at 50°C for 10 min with stirring and then cured at RT for 24 h. The samples were designated as S1 (no solvent), S2 (acetone), S3 (ethanol) and S4 (DMF). SEM images of the fracture surfaces of various samples showed no significant difference in the state of dispersion. However, the diameters of the SWCNTs varied from sample to sample. The number of SWNT bundles pulled out from the epoxy matrix was on the order of S2 > S3 > S4, showing ethanol and DMF to be better choices for CNT dispersion.

Rajoria and co-workers [Rajoria et al., 2005] prepared the fabrication of epoxy composites with SWCNTs and MWCNTs following the same method. Poor adhesion between SWCNTs and matrix was observed from the SEM image in this case. Fidelus et al. [Fidelus et al., 2005] used randomly oriented SWCNTs (HiPco, diameter 0.8–1 nm) for the preparation of epoxy composites employing procedure similar to that used for MWCNTs. Moisala et al. [Moisala et al., 2006] also reported the fabrication of SWCNT- and MWCNT-based epoxy composites using the same procedure.

Bryning et al. [Bryning et al., 2005] used two types of SWCNTs: (a) laser synthesized (length 230–802 nm, diameter 1.2–1.5 nm) and (b) HiPco (length 79–257 nm, diameter 0.8–1.4 nm) with different aspect ratios in epoxy polymer employing two different processing methods. 0.004 wt% pure SWCNTs were ultrasonically dispersed in DMF. SWCNT/DMF suspension was added to epoxy resin (Epon 828), and the mixture was sonicated for 4 h at 80°C. Epikure 3234 curing agent was then added, and the mixture was sonically stirred for 2 min. The samples were divided into two batches and one batch was cured at 90°C for 30 min in a water bath without sonication (non-sonicured) while the other batch was cured at 80°C in a sonicator bath (sonicured). The cured samples were annealed at 120°C for 2 h. The SEM of the non-sonicured samples showed re-aggregation of SWCNTs, while the sonicured samples showed that the SWCNT dispersion was quite homogeneous.

In another work, Hadjiev et al. [Hadjiev et al., 2006] reported the use of ODA-functionalized SWCNTs for the synthesis of epoxy-SWCNTs composites. SWCNTs produced by the laser ablation technique [Arepalli et al., 2004] were purified [Chaiang et al., 2001] and treated with concentrated H_2SO_4 , 30% H_2O_2 mixture at 70°C for 20 min. The SWCNTs were refluxed with ODA at 110°C for 40 h. Excess amine was removed by sonication and washing with ethanol and THF. The suspension of ODA-SWCNTs in 70% acetone/30% toluene was mixed with epoxy resin Epikote 862. After removing acetone, Epikure W was added, and the mixture was stirred well. The composite was vacuum dried for 2 h at 60°C and molded. This was followed by annealing at 80°C for 30 min in a vacuum oven. The curing cycle involved an annealing at 121°C for 1 h and at 175°C for 2 h. TEM images showed the presence of SWCNTs with physisorbed ODA molecules in the epoxy matrix. The embedded tubes appeared to have a bent structure.

Wang and co-workers [Wang et al., 2006] proposed an effective amino functionalization through diazotisation of SWCNTs for reinforcing epoxy polymer composites. About 50 mg of pristine SWCNTs was dispersed with 50 ml DMF under sonication to which 7.366 g Epikure-W curing agent was added followed by 2.7 ml isoamyl nitrite. The mixture was heated to 80°C for several hours, diluted with DMF, filtered and washed with DMF. The DMF was removed with ether, and the CNT membrane was vacuum dried at 65°C for 10 h. The CNT membrane was made into a paste with acetone. The excess acetone was removed, and the required amount of EPI-W was added. The mixture was transferred to the epoxy resin diluted with acetone, which was sonicated for 10 h under ice-cooling. The composite was dried under vacuum and cured in a hot press at 177°C for 2.5 h. The subsequent post-cure was done at 177°C for another 2 h. Fig. 26 shows the AFM image of grafted SWCNT-epoxy composite section under tapping mode. The AFM image of the composite section showed high embedding and uniform dispersion of functionalized SWCNTs throughout the epoxy matrix.



Fig. 26. AFM image of grafted SWCNT-epoxy composite section under tapping mode. Reproduced from Wang et al., 2006.

Tao et al. [Tao et al., 2006] demonstrated a simple method to fabricate epoxy composites. Three different grades of SWCNTs; short SWCNTs (S-SWCNT with diameter 0.8–1.6 nm, length 500 nm), HiPco-SWCNTs (diameter 3–5 nm) and XD-grade CNTs (XD-CNT), which was a mixture of single, double and triple-walled CNTs were used in the study. About 1 g of Epikote 862 and 0.264 g of Epikure W were mixed with 1 wt% of CNTs in a mortar and pestle for 30 min. Surface morphology analyzed by SEM showed good dispersion and distribution of CNTs. The nanotube wetting was relatively better with HiPco SWCNTs.

In another work, Li and his group [Li et al., 2006, Huang et al., 2007] used SWCNTs with different aspect ratios for fabricating SWCNT-epoxy composites. Arc discharge-produced SWCNT-long, SWCNT-short and annealed SWCNT-short were used in this study. A commercially available bisphenol A-type epoxy resin (618 type) and an amine-type hardener $[C_{17}H_{31}CONH(C_2H_4NH)_2H]_2$, were used to prepare the polymer matrix at the ratio 2:1. SWCNTs were first dispersed in acetone by ultrasonication at RT for 2 h, and to this suspension epoxy resin/acetone solution was added. The mixture was again sonicated for 2 h, and hardener was added during mechanical stirring. The mixture was further sonicated for 15 min, molded and cured at RT overnight. SEM showed nice dispersion of SWCNTs in the matrix.

Lau et al. [Lau et al., 2006], in another work, compared the reinforcing effect of CVDsynthesized SWCNTs [Li et al., 2006 b] with coiled CNTs [Lu et al., 2004] in an epoxy matrix. Nanotubes were initially dispersed into ethanol with strong sonication for 1 h. The desired amount of epoxy resin (Araldite GY 251) was added, and the mixture was sonicated again for 1 h. Solvent was removed, and the mixture was degassed in vacuum for 4 h. After adding the hardener (CIBA HY 956), the mixture was molded and cured with stirring at RT for 24 h. Comparison of the SEM images of the composites indicated good anchoring of coiled nanotubes to the matrix, while poor adhesion leading to large holes in the matrix was observed for SWCNTs.

On the other hand, Liu et al. [Liu et al., 2007] reported, for the first time, the clay-assisted dispersion of SWCNTs in epoxy polymer. In a typical preparative method, HiPco-produced SWCNTs and unmodified natural montmorillonite clay (Cloisite[®]Na⁺, CEC = 92.6 meq/100 g) were first suspended in 40 ml acetone with sonication for 20 min. Epoxy resin (D.E.R. 354), curing agent (ECA-100) and amine catalyst (N,N-Dimethylbenzylamine) were then dissolved in acetone and mixed with the SWCNT-clay suspension. This mixture was mechanically stirred for 5 min at 1720 rpm and then for 30 min at 3100 rpm followed by sonication in a water bath for 1 h. The acetone was removed, and the mixture was cured for 1 h at 95°C followed by 3 h at 150°C. Significant improvement in SWCNT dispersion was observed for samples containing clay from optical microscopy and SEM images.

Wang et al. [Wang et al., 2007] modified and integrated SWCNTs into the epoxy matrix through covalent and non-covalent functionalization. Selected methods, including oxidization, polymer wrapping, and mechanical chopping were used to functionalize HiPco-produced SWCNTs (diameter 0.8–1.2 nm, length 100–1000 nm). Oxidation (o-SWCNTs) involved stirring SWCNTs with concentrated H₂SO₄ acid for 1 h, washing and drying. In polymer wrapping, SWCNTs were magnetically and ultrasonically stirred with gum arabic, filtered and dried (GA-SWCNTs). In mechanical chopping, SWCNTs (c-SWCNTs) were dispersed in Triton-X 100, washed with isopropanaol and chopped with a diamond knife. Functionalized SWCNTs were made into a paste with acetone. The curing agent DETDA was added to the functionalized SWCNT paste and sonicated for 30 min under ice cooling. The solution was mixed with epoxy resin (Epon 862) diluted with

acetone using sonication for 3.5 h under ice cooling along with magnetic stirring. The mixture was dried in vacuum for 10 h, molded and cured in a hot press at 177°C for 2.5 h. The subsequent post cure was conducted at 177°C for another 2 h. SEM characterization showed a smooth surface for the neat resin. The raw SWCNTs gave non-uniform distribution in the matrix. All the functionalized SWCNT-epoxy composites revealed rougher surfaces due to better dispersion of CNT network.

Lucas et al. [Lucas et al., 2007] in another work used 0.05 wt% of HiPco SWCNTs to reinforce the epoxy matrix. A mixture of SWCNTs hardener HY5052 was first sonicated for an hour and then magnetically stirred for 30 min. After the addition of epoxy resin LY5052, the mixture was manually stirred for 5 min, molded and degassed in vacuum for 30 min. The cold-cured sample was prepared by leaving the composite to cure at RT in air for 7 days, while the hot-cured samples were prepared by leaving the mould in an oven overnight at a fixed temperature (40–150°C).

Bekyarova et al. [Bekyarova et al., 2007b] demonstrated the fabrication of hybrid epoxy composites with acid-functionalized SWCNTs (arc-discharge) by the infiltration method reported with MWCNTs [Bekyarova et al., 2007a]. 0.2 and 0.5 wt% of acid-functionalized SWCNTs (SWCNT-COOH) were mixed with Epon 862 and the curing agent Epikure W. This solution was infused with carbon fibre using VARTM technique for 1 min. After the infiltration, the specimens were cured for 6 h at 130°C under vacuum. SEM images showed rougher surfaces for SWCNT containing samples.

Wang and co-workers [Wang et al., 2008] used an *in situ* functionalization method to graft epoxide onto SWCNTs' outer surfaces and improve the integration of SWCNTs into the epoxy matrix. HiPco SWCNTs were ground with three drops of benzene and dispersed into glycidyl methacrylate (GMA) by sonication. The mixture was then stirred with benzoyl peroxide (BPO) and heated to 75°C for 24 h under strong stirring. The mixture was diluted with benzene and filtered, washed with acetone (repeated three times) and annealed at 60°C for 10 h. The resultant epoxy-grafted SWCNT (g-SWCNTs) membrane was ground to a paste with chloroform. The curing agent was added to the g-SWCNT paste and mixed with chloroform. The epoxy resin was diluted and added to the SWCNT suspension, which was sonicated for 3 h. Finally, the mixture was placed under high-speed shearing at 2000 rpm for 3 h. The resultant composite mixture was vacuum dried for 12 h, molded and cured in hot press at 177°C for 2.5 h. The subsequent post-cure was conducted at 177°C for another 2 h. Composite samples were prepared with 0.5 and 1 wt% SWCNT loading.

The fracture cross section of the samples examined by SEM showed very good dispersion of g-SWCNTs in the epoxy matrix with no apparent agglomeration. However, pristine SWCNTs formed large agglomerates in the composite.

Valentini et al. [Valentini et al., 2008] demonstrated how the grafting of butylamine onto CF_4 plasma-treated SWCNTs is used to obtain a cross-linked epoxy composite. SWCNTs (length 50 nm–1 µm, diameter 0.8–2 nm) were subjected to plasma-assisted fluorination [274] to get F-SWCNTs. F-SWCNTs were ultrasonically dispersed in liquid butylamine for 30 min using a thermostatic bath at 5°C. The F-SWCNT grafted with butylamine (BAM-SWCNTs), were then added to epoxy resin DGEBA. The same procedure was adopted to prepare a composite with un-modified SWCNTs (BAM-u-SWCNTs). SEM images in this case also showed better dispersion with amine functionalized nanotubes.

Wang et al. [Wang et al., 2008] produced an SWCNT-epoxy composite using the solution casting technique. SWCNTs from arc-discharge (diameter 1.2–1.5 nm, length >2 μ m) were purified by treating with concentrated HNO₃ at 80°C for 1 h to eliminate impurities. Acid-

treated SWCNTs were dispersed in ethanol and sonicated for 30 min. Different SWCNT weight fractions were then mixed with epoxy resin (E-51) under sonication for 2 h. Hardener N,N-benzyl dimethyl amine (BDMA) was added into the mixtures in two steps: Half of the BDMA was added into the nanotube/epoxy mixtures before stretching, and the mixture was sonicated and stirred at 1500 rpm simultaneously again for 1 h. The other half of the BDMA was added after a repeated stretching process. The SWCNT-epoxy composite was then stretched along one direction at a draw-ratio of 50 and then folded along the same direction and stretched repeatedly 100 times at ambient atmosphere manually at a speed of 0.5 m/s for 30 min. The film samples were compressed under a pressure of about 10 MPa for 5 min using a hydraulic press. All samples were kept in vacuum at RT for 7 days. SEM micrographs demonstrated that SWCNTs were well aligned along the stretching direction.

2.2.2 Thermal and mechanical properties

Using Raman spectroscopy, the deformation of SWCNTs produced by different methods in the epoxy matrix was studied by Cooper et al. [Cooper et al., 2001]. The second order Raman peak at 2640 cm⁻¹ which is a measure of load transfer was shifted significantly to a lower wavenumber (~13 cm⁻¹/% strain) for composite with SWCNT-P when compared to the one SWCNT-A. This demonstrated better reinforcing ability of laser produced SWCNTs. Based on the strain-induced Raman shift, the modulus of SWCNTs was calculated as 1 T Pa, which was higher than that for MWCNTs. Puglia et al. [Puglia et al., 2003a, Puglia et al., 2003b] observed up-shifted Raman peaks for composites containing 5 wt% of SWCNTs.

The peak shift was significant for the radial breathing mode (RBM), which is dependant on the tube diameters [Rao et al., 1997, Eklund et al., 1995]. The shift represented intercalation of resin with CNTs during the curing reaction, which exerts pressure on the dispersed nanotubes and changes the vibrational frequencies. The rate of the cure reaction and thermal degradation increased with SWCNT content up to 5 wt% above which there was no Individual nanotubes were well dispersed in the matrix, which pronounced effect. contributed to the higher surface for heat propagation. Similar results were reported by Valentini et al. [Valentini et al., 2004]. Hadjiev et al. [Hadjiev et al., 2006] also reported an upshift of Raman bands for composite containing ODA-functionalized SWCNTs. RBM intensities of SWCNTs in epoxy matrix with applied strain has been investigated by Lucas et al [Lucas et al., 2004]. The intensity measurements on the composite with 0.025 wt% SWCNTs (strain between -0.6 and 0.65) showed that some peaks increased the intensity while others decreased depending on the chirality and diameter. In another work, the same group [Lucas et al., 2007] demonstrated the up-shift of RBM bands for epoxy composites as a function of curing temperature.

Zhu and co-workers [Zhu et al., 2003] reported improved mechanical properties for composites prepared with fluorinated SWCNTs. Epoxy composites with 1 wt% functionalized nanotubes showed 18 and 24% improvement in tensile strength and modulus respectively when compared to the resin with unmodified SWCNTs. Over the neat resin, the modulus of these specimens showed a 30% increase. Fluorinated nanotubes were well dispersed in the matrix, showing good interaction with the epoxy matrix thereby reinforcing the polymer. Miyagawa et al. [Miyagawa et al., 2004; Miyagawa et al., 2005] also reported dramatic improvement in storage modulus for epoxy composites with a very small amount of fluorinated SWCNTs. The modulus increased by 1.1 GPa with the addition of only 0.3 wt% of FSWCNTs, representing a 33% improvement. Brown et al. [Brown et al., 2005] also

reported 30–40% improvement in storage modulus with very low CNT content of 0.1 wt%. The reinforcing effect of small SWCNT content 0.05–0.1 wt%) was observed by Liu et al. [Liu et al., 2007] as well.

Ren et al. [Ren et al., 2003] demonstrated the good potential of SWCNTs as reinforcing filler and evaluated the fatigue strength of SWCNTs in epoxy as twice as that of CF-based composites. Gou et al. [Gou et al., 2004] studied the mechanical properties of HiPco SWCNT-reinforced epoxy matrix. The DMA results (refer Fig. 27) showed an increase in composite storage modulus with the introduction of CNTs. A 250–300% increase in storage modulus was observed with the addition of 20–30 wt% nanotubes below T_g .

The damping characteristic of SWCNT-epoxy composites prepared by ultrasonication was investigated by Zhou et al. [Zhou et al., 2004]. For samples with SWCNTs, damping



Fig. 27. Storage moduli of SWCNT-epoxy composites. Reproduced from Gou et al., 2004.



Fig. 28. (a) Storage modulus and (b) Tg's of the composites. Reproduced from Liao et al., 2004.

increased with strain up to 1 wt% CNTs and then decreased. The concept of "stick and slip" frictional motion could effectively explain the observations. Rajoria et al. [Rajoria et al., 2005] reported similar results on the damping properties of MWCNT-epoxy composites. Higher damping for SWCNT-epoxy composite was also observed by Wang et al [Wang et al., 2004]. The effect of various SWCNT dispersion process (Table 8) on the mechanical properties of epoxy was reported by Liao et al [Liao et al., 2004]. DMA results of SWCNT/SC-15 composites thus obtained are summarized in Fig. 28. From the results, only tip sonication was found to consistently improve nanotube dispersion and mechanical properties. The highest storage modulus was observed for Sample 3 (50.8% when compared to the neat resin) which was fabricated by using tip sonication in the presence of acetone and with only 0.5 wt% of CNTs. All the samples with nanotubes except sample 2, showed lower T_g than that of pure epoxy. Sample 2 and the neat resin were prepared without using surfactant or solvent, so the decrease in T_g for the other samples was attributed to the surfactant or solvent effect. Linear decrease in Tg with increase in fluorinated SWCNT content was also reported by Miyagawa et al [Miyagawa et al., 2004]. A detrimental effect of clay on $T_{\rm g}$ of SWCNT-epoxy was demonstrated by Liu et al. [Liu et al., 2007] where the samples without clay showed increase in T_g values when compared to neat resin. Wang et al. [Wang et al.,2004] observed no obvious change in Tg for composites with varying SWCNT content prepared by the infiltration method. Brown et al. [Brown et al., 2005] also reported unchanged T_{g} values for the composites.

On the other hand, Li et al. [Li et al., 2004] used AFM to study the hardness, elastic modulus and scratch resistance of SWCNT-epoxy composites. Epoxy with 5 wt% SWCNTs loading showed an increase in the elastic modulus by 75% and hardness by 30% in comparison to the pure epoxy matrix. The storage modulus and the loss modulus also increased with increasing CNT-content. However, composites with 3 and 5 wt% SWCNT showed debris particles and cracks inside or around the scratch tracks for the scratch tests due to the presence of CNT agglomerates. Wang et al. [Wang et al.,2004] noticed an increased storage moduli for the SWCNT-epoxy composites which was less than that predicted due to poor load transfer as a result of dispersion effects. They observed no regular trend in mechanical properties with CNT-content.

The influence of SWCNT dispersion on mechanical properties of epoxy was studied by Song et al. [Song et al., 2005]. Epoxy composites with poorly dispersed CNTs showed higher storage and loss modulus due the presence of larger agglomerates that can trap polymer in the void reducing volume fraction of polymer matrix. However, improved tensile strength and elongation at break were observed in the case of composite with good CNT dispersion. Thermal conductivity was higher for samples with well-dispersed CNTs which showed an increasing trend with nanotube amount. Moisala et al. [Moisala et al., 2006] in contrast observed a decrease in thermal conductivity for epoxy composites with SWCNT addition.

Lau and co-workers [Lau et al., 2005] dispersed SWCNTs in an epoxy matrix using various solvents and studied the thermal and mechanical properties of the resulting composites. In comparison with the pure epoxy sample S1, the hardness value of acetone-dispersed sample S2 increased slightly, while the hardness values of the ethanol-dispersed sample S3 and the DMF-dispersed sample S4 decreased (more pronounced decrease for DMF sample of about 56% with neat resin). A relatively higher amount of residual solvent resulted in poor mechanical properties of S3 and S4.

Fidelus et al. [Fidelus et al., 2005] used two different epoxy polymers (Epon 815 and LY 564) and randomly oriented SWCNTs (0.01 to 0.5 wt%) for the preparation of epoxy composites.

Below 50°C, only moderate increase in storage modulus and decrease in T_g were observed for both series with respect to the pure matrix. On the other hand, a substantial increase in impact strength (18 and 35%, respectively, for LY 564 and Epon 815) was measured with the loading range. MWCNTs showed better reinforcing effect than SWCNTs.

Wang and co-workers [Wang et al., 2006] demonstrated reinforcement of epoxy polymer by amine-functionalized SWCNTs. Fig. 29 shows typical DMA results of SWNT-epoxy composites. Composite containing amine-functionalized SWCNTs showed a noticeable increase in storage modulus compared to those with pristine SWCNTs and neat resin. The storage modulus of the epoxy increased from 2.44 to 3.04 GPa with 0.5 wt% of functionalized CNTs (24.6% improvement). At the same time, introduction of the same amount of pristine CNTs could produce only a 3.2% improvement in modulus. Tg values were 170, 164 and 158°C for pure epoxy, pristine SWCNT-epoxy and functionalized SWCNT-epoxy, respectively. In another work [Wang et al., 2008], they used epoxide-grafted SWCNTs (x-SWCNTs) in strengthening the epoxy matrix. Similar trends in storage modulus and $T_{\rm g}$ were reported. Valentini et al. [Valentini et al., 2008] proposed plasma fluorination followed by amine treatment as an effective functionalization procedure for SWCNTs to obtain better dispersion in epoxy. However, the tensile strength and elongation at break were lower for BAM-u-SWCNTs-epoxy composite with respect to the pure resin. At the same time, incorporation of CNTs (both functionalised and pristine) showed a positive effect on elastic modulus.



Fig. 29. Typical DMA results of SWNT-epoxy composite. Reproduced from Wang et al. 2008 Lau et al. [Lau et al.,2006] compared the mechanical properties of composites reinforced with SWCNTs and coiled CNTs at the same nanotube concentration of 2 wt%. Coiled CNTs were found to superior to SWCNTs in hardening the matrix by about 3 times. Flexural strength of composite with coiled tubes was also higher due to the good mechanical locking between coiled tubes and the polymer.

The promising role of SWCNTs functionalized by different method in reducing CTE of epoxy composite was demonstrated by Wang et al. [Wang et al.,2007]. CTE values of the

neat epoxy resin and nanocomposites below the *T*g range are presented in Fig. 30. All the composites showed lower T_g than the pure polymer. The reduction in CTE value for p-SWCNT-epoxy was not that significant when compared to those with functionalized SWCNTs. From the results, it is clear that the reduction in CTE values depends on the functionalization method. Substantials decreases in CTE values 52.4, 42.4 and 13.9% were observed for c-SWCNT (chopped SWCNTs)–epoxy, o-SWCNT (oxidized SWCNTs)–epoxy and w-SWCNT (polymer-wrapped SWCNTs)–epoxy, respectively.



Fig. 30. CTE values of the neat epoxy resin and composites below the *T*g range. Reproduced from Wang et al., 2007.

The mechanical performance of hybrid epoxy composite containing acid-functionalized SWCNTs was reported by Bekyarova et al. [Bekyarova et al., 2007b]. The flexural strength of the composite showed no significant improvement with the introduction of SWCNTs. However, the shear strength showed 20 and 40% increases with the incorporation of 0.2 and 0.5 wt% SWCNT-COOH.

Wang et al. [Wang et al., 2008] reported significant improvement in mechanical properties for composites with aligned SWCNTs. 3 wt% loading of SWCNTs showed significant improvement in the tensile strength (8–21.1 MPa) and Young's modulus (415–843 MPa). Tensile strength decreased at higher CNT weight fractions larger than 6 wt%.

2.2.3 Electrical properties

The conducting properties of SWCNT-epoxy composites have been investigated by Barrau et al [Barrau et al., 2003 b]. According to the observations, the D.C. conductivity increased as a function of CNT weight fraction (0–2.5 wt%). A dramatic increase in conductivity was observed between 0.2 and 0.4 wt% of CNTs, and the percolation threshold was calculated as 0.3 wt%. The conductivity increased with temperature below the percolation threshold, and above the threshold it was independent of temperature for all the CNT contents. The effect of palmitic acid on the conductivity for the same epoxy system was studied in another work [Barrau et al., 2003 a]. Fig. 31 shows the comparative plot of the dc conductivity dependence

on the CNTs content at RT(\bullet) with palmitic acid at 1:1 CNTs to C₁₆H₃₂O₂ weight ratio and (\circ) without palmitic acid. Higher conductivity was measured for composites with palmitic acid in comparison to pure resin and the composite without palmitic acid, and the conductivity was observed to be dependent of the surfactant concentration. The composite with 1:1 CNT/palmitic acid ratio showed the highest conductivity, which is attributed to better CNT dispersion. The percolation threshold was between 0.05 and 0.1 wt% of CNTs.



Fig. 31. Comparative plot of the dc conductivity dependence on the CNTs content at $RT(\bullet)$ with palmitic acid at 1:1 CNTs to $C_{16}H_{32}O_2$ weight ratio and (\circ) without palmitic acid. Reproduced from Barrau et al., 2003a.

Valentini et al. [Valentini et al., 2004] reported an increase in dielectrical properties of SWCNT-epoxy composites with the incorporation of SWCNTs as conductive fillers.

Brown et al. [Brown et al., 2005] measured the A.C. conductivity for SWCNT-epoxy matrix. According to the results, the composite showed very low conductivity at 0.01 wt% of CNTs very similar to that of pure epoxy polymer. As the CNT content was increased to 0.1 wt%, the composite became more conductive. A jump in conductivity value was observed between 0.01 and 0.05 wt% of CNTs (percolation threshold). These results were consistent with the work of Barrau et al. [Barrau et al., 2003 a]

Song et al. [Song et al., 2005] reported the electrical conductivity of composites with different degrees of dispersion of SWCNTs. Introduction of CNTs to the matrix increased the conductivity up to 1.5 wt% of CNTs. The conductivities of composites with well-dispersed SWCNTs were slightly higher than those with poor dispersion. A percolation threshold less than 0.5 wt% was observed for both series of composites.

Very low threshold concentration [5.2 (\pm 1.9/-0.5) × 10⁻⁵] for non-sonicured laser oven SWCNT-containing epoxy composite was proposed by Bryning et al. [Bryning et al., 2005] This was 2-fold lower than the corresponding HiPco SWCNT-epoxy composite. The sample without sonication showed aggregation of CNTs which contributed the rapid percolation. Li et al. [Li et al., 2006, Huang et al., 2007] reported a percolation threshold of 0.062 wt% for composites with SWCNTs with high aspect ratio. With short-SWCNTs and annealed-short-SWCNTs, the threshold concentrations were 0.318 and 0.342 wt%, respectively.

In another work, Moisala et al. [Moisala et al., 2006] measured the percolation threshold for SWCNT-epoxy composites as 0.05–0.23 wt%, which was higher than that observed for MWCNTs (0.005 wt%). An increase in electrical conductivity for epoxy composites was also observed by Liu and co-workers [Liu et al., 2007]. Addition of 0.2 wt% of clay to the system containing 0.05 wt% of SWCNTs dramatically increased the conductivity. Furthermore, the percolation threshold of the epoxy composites was reduced 0.05 wt% SWCNTs to 0.01 wt% SWCNTs with the introduction of clay.

Valentini et al. [Valentini et al., 2008] demonstrated an increase in electrical conductivity for composites with amine-functionalized SWCNTs. Wang et al. [Wang et al., 2008] showed the effect of CNT alignment on electrical conductivity. The conductivity measurements with CNT content showed that very small amounts of aligned SWCNTs are enough to obtain significant enhancement in electrical conductivity. The percolation threshold along the stretching direction was observed to be lower than the value perpendicular to the SWCNT orientation.

2.3 DWCNT-containing epoxy composites

Gojny et al. [Gijny et al., 2004] fabricated epoxy composites with increased mechanical properties with amine-functionalized DWCNTs by the calendering technique. The matrix was epoxy resin (MGS L135i) together with the amine-curing agent H 137i. Pure or amine-functionalized DWCNTs (0.1 wt%) were used to reinforce the epoxy resin. CNTs were manually mixed into the resin, and in the following step, a three roll calander was used. The dwell time of the CNT-EP suspension on the rolls was approximately 2 min while nanotubes were dispersed in the resin by the enormous shear forces. The suspension was collected, mixed with the hardener for 10 min by stirring, cured for 24 h at RT and finally post-cured at 60°C for 24 h. For comparison, samples containing the DWCNTs (as-received and amino-functionalized) were mixed with the amine-curing agent, sonicated for 10 min and cooled to RT. The resin was added under stirring, and the mixture was sonicated again under the given conditions but cooled in a water bath to avoid an untimely curing. Finally, the composite was cured for 24 h at RT followed by a 24 h at 60°C post-curing.

TEM and SEM images of the achieved distribution of DWCNTs and amine-functionalized DWCNTs in the epoxy matrix by the use of a calander showed homogenous distribution and exfoliation of CNTs over the composites prepared by sonication method. The Young's modulus of the composites increased with the introduction of nanotubes. Composite with amine-functionalized DWCNTs showed higher modulus when compared to the non-functionalized DWCNTs. All composites had a significantly higher fracture toughness compared to the neat epoxy.

Li et al. [Li et al., 2006] also prepared epoxy composites with well aligned DWCNT strands by the solution mixing method. The aligned DWCNTs were prepared by the CVD method [Li et al., 2005]. The epoxy resin (E-44) and polyamide hardener (volume ratio 2:1) were successively dissolved in acetone. DWCNT strands were then immersed into the solutions for 1 min. The composite fibres were dried and cured completely for 7 days at RT.

Good interfacial bonding between the polymer and filler was revealed by TEM analysis. Compared to DWCNTs, the composite showed significant improvement in tensile strength and Young's modulus (25% and 75% respectively). The second-order Raman peak was down-shifted for the composite showing effective load transfer.

An epoxy system containing carboxy DWCNTs (C-DWCNTs) functionalized with Nmethyldiethanolamine (MDEA) has been investigated by Terenzi and co-workers [Terezeni et al., 2008]. The polymeric matrix of the composite was obtained from a DGEBA epoxy resin and a solid MDEA. The C-DWCNTs were stirred in the MDEA at the melting temperature of the amine (i.e., 100°C for 45 min). 1 wt% of MDEA/C-DWCNTs, were added to epoxy. Another preparation method of first mixing the C-DWCNTs with epoxy and then adding the MDEA moiety was also used.

The SEM analysis of the fracture surface indicated very good nanotube dispersion and homogeneity for the sample with MDEA-functionalized DWCNTs. The calorimetric results showed that addition of CNTs increased the curing rate, and this effect was maximum for functionalized DWCNTs.

Gojny et al. [Gojny et al., 2005], in another work, studied the mechanical and electrical properties of epoxy matrix reinforced with DWCNTs and amine-modified DWCNTs. The composites were manufactured via the resin transfer molding (RTM) process. The CNTs were manually added to the resin (L135i) system. This was further mixed with a shear mixer at a gap setting of 5 μ m at speeds of 20, 60 and 80 rpm for the first, second and third rolls, respectively, with a dwell time of 2 min. The suspension was then stirred for 10 min with the hardener H137i and cured at RT for 24 h followed by a post cure at 60°C for another 24 h. The mixture was then infused with the glass fibre by RTM and cured as described previously. The post curing was done at 80°C for another 24 h.

The interlaminar shear strength of the glass fibre-reinforced polymer showed noticeable increase by 20%, whereas the tensile properties remained unaffected. The electrical properties were anisotropic in nature. The conductivity measured in plane was much higher that that obtained for out of plane, which was attributed to the conduction paths by CNTs located between the matrix channels of glass fibre. ributed to the conduction paths by CNTs located between the matrix channels of glass fibre.

2.4 CSCNT-containing epoxy composites

The effect of the dispersion, ozone treatment, and loading of CSCNTs on mechanical, electrical and thermal properties of the epoxy-CSCNT composites were investigated by Choi et al [Choi et al., 2005]. CSCNTs (diameter 60–100 nm, length 20–40 nm) were prepared by floating catalyst [Tibbettes et al., 1993]. CSCNTs were oxidized with ozone at RT for 1 h and dried at 100°C for 12 h. To prepare the composites, the CSCNTs (0, 5, 10 and 20 wt%) were dispersed in acetone by sonication, added to the epoxy resin and stirred at RT at 600 rpm for 15 min. After evaporating the acetone, the mixture was vacuum dried at 80°C for 30 min. The hardener was then blended into the mixture at RT for 10 min. The mixture was kept under vacuum at RT again for 10 min. Samples were cured at RT for 16 h followed by 120°C for 3 h.

SEM images of the fractured cross section of the composites containing untreated and ozone-treated CSCNTs showed no difference in the dispersion states except for the presence of more voids in the composites with untreated CSCNTs. TEM observation under low magnification revealed nanotube aggregates in both the untreated and treated composites. The ozone-treated CSCNTs showed better wetting in the epoxy matrix. The electrical conductivity increased with increasing CSCNT content. No significant effect of ozone treatment was observed on electrical conductivity. Tensile strength and Yong's modulus for both series of composites were almost similar. The coefficient of friction was lower for the
composites when compared to the pure epoxy where the ozone-treated CSCNT sample gave the lowest value. Measurement of thermal properties indicated that the heat resistance of the composites increased with CSCNT loading regardless of ozone treatment. Composites with untreated and ozone-treated CSCNTs showed an increase in T_g (drastic increase with ozone treated CNTs), and the magnitude decreased with CNT-content.

Yokozeki et al. [Yokozeki et al., 2007] investigated the matrix cracking behaviors in carbon fibre-epoxy laminates filled with CSCNTs. The CSCNTs used in this study were synthesised by a floating reactant method [Liu et al., 2001] with aspect ratio 10. A two-step mixing procedure was employed; EP827 epoxy and CSCNTs (0, 5 and 12 wt%) were combined using the planetary mixer at 70°C, and then, CSCNTs were dispersed using the wet mill at 70°C for 45 min. The blended CSCNT-dispersed epoxy was diluted with EP827, and the dicyandiamide curing agent was added to the compounds. A wet coater was used to impregnate the carbon fibres with the resin.

The introduction of CSCNTs resulted in stiffness and tensile strength improvement in the 90° direction. The highest values were obtained for the sample with 5 wt% CSCNT content. Retardation of matrix crack formation was clearly observed in CSCNT-dispersed resin laminates with 40% improvement in fracture toughness. SEM images showed rougher surfaces for composites.

3. Conclusions

Recently, much attention has been paid to the fabrication of reinforced composites where the reinforcement filler size has reduced to nanometer range. These engineering materials are expected to have high strength-weight and modulus-weight ratios when compared to the normal commercial polymer composites where microscale particles are incorporated. Among various nanoreinforcements used today, CNTs are considered as potential fillers for the composites to improve mechanical, electrical and thermal transport due to their remarkable structure dependent properties. However, two issues concerning the effective improvement of composite properties are the interfacial bonding and uniform dispersion of the tubes in the polymer matrix. In addition, the conventional mechanisms and theories explaining the effect of filler on structural, mechanical and physical properties may not applicable to CNTs and other nano-fillers.

From the existing literature, considerable effort has been given to the synthesis and processing of CNT-reinforced epoxy composites. The modification of epoxy resins with CNTs could endow the materials with some superior properties such as broadening of $T_{g'}$ significant increases in mechanical properties and substantial improvement in thermal and electrical conductivity. The reports published so far on these materials focus on investigating whether a CNT-modified epoxy matrix yields improved properties with neat epoxy as the matrix material. Except a few reports, most of the published work advocates surface functionalization of CNTs and use of a surfactant as possible routes to enhance the dispersion and interfacial adhesion between CNTs and epoxy matrix. Various types of CNTs with or without physical and chemical modifications were utilized to fabricate the composites to make them effective fillers regarding mechanical properties—especially toughness—and the properties of the resulting composites were also analyzed.

However, the extent of homogeneous dispersion is found to be dependent on the aspect ratio, volume fraction, CNT entanglement, matrix viscosity and inter-tubular interactions. Different methods including sonication, stirring and calendering have been proposed for the preparation of composites where some of the reports contradict each other in the effectiveness to get uniform CNT distribution. Though the CNT-reinforced epoxy has been shown to be a possibility, realising the properties of individual CNTs in assemblies of CNTs is a formidable challenge. An efficient exploitation of CNTs as structural elements is generally related to the degree of dispersion, impregnation with matrix and the interfacial adhesion. Much work remains to be performed in order to understand how the nano-reinforcement results in major changes in material properties.

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Energy Dissipation Capacity in MWCNTs Reinforced Metal Matrix Nanocomposites: An Overview of Experimental Procedure

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1. Introduction

Adsorption of vibration energy by mechanical damping is a significant problem in many engineering designs. High damping materials are used to reduce vibration in aircraft and other machinery. The benefits of damping treatment are advanced durability, reliability and service life of components, reductions in weight, noise and costs (Chung, 2001).

By invoking the properties of nanostructures it may be possible to control the shock wave propagation in the material and thus, significantly enhance the impact energy dissipation; however, only limited research papers concern about damping composite structures and shock resistant of nanomaterials.

If one goes to the nanoscale, the damping levels/dynamics of structures are mostly unknown and require extensive investigations. This chapter traces the experimental and analytical investigation methods for damping capacity and its application to nanocomposites.

A couple of works were published about investigation of damping capacity in different material (Koizumi et al., 2003; Gu et al., 2004; Srikanth & Gupta, 2005; Zhang et al, 2005; Botelhoa, 2006; Kireitseu et al., 2007; Yadollahpour et al., 2009). These works were summarized in Table 1. The first part of this chapter deals with an overview of experimental procedures for investigation of energy dissipation capacity in materials.

Carbon nanotubes (CNTs) have superior mechanical properties with an elastic modulus up to 1 TPa and a tensile strength up to 150 GPa and, as well as excellent thermal stability and electrical conductivity (Ci et al., 2006). Their exceptional mechanical properties make CNTs ideal candidates as reinforcements in composite materials to increase both stiffness and strength, while contributing to weight savings (Esawi & Morsi, 2007). Larger portion of the researches have been focused on the development of CNT reinforced polymer, ceramic based composites, and only a few studies have been concerned with the manufacture of CNT reinforced metal matrix composite (George et al., 2005;Chunfeng et al., 2007). It has been confirmed that the mechanical properties of metal matrix composites were improved, when an appropriate amount of nanotubes were added (Deng et al., 2007a). Beside considerable reinforcement effect of CNTs, fabrication of MMCs with nanostructured matrices may also provide excessive properties due to their greater mechanical characteristics compared to coarse-grained counterparts.

Author	Year of publication	Material	Experimental method for energy dissipation measurement
Y. Koizumi et al.	2003	ultra-fine grained aluminum produced by ARB	free-decay method by a torsional pendulum apparatus
Z. Zhang et al.	2005	AZ91D magnesium alloy	Dynamic mechanical analyser (DMA)
M. Kireitseu et al.	2007	carbon nanotube- reinforced UHMW-PE polymer composite	vibration shaker tests with clamped specimen
E.C. Botelho et al.	2006	Fiber-metal laminate (FML) composites	free vibration test and the frequency response function (FRF) analysis
J. Gu et al.	2004	aluminum matrix composites reinforced with coated carbon fibers	dynamic mechanical thermal analyser (DMA 2980)
N. Srikanth et al.	2005	aluminium based composites Ti particulates as reinforcement	impact-based "Suspended" beam based on the ASTM C1259-98 standard
M. Yadollahpour et al.	2009	Al-Zn/α-Al2O3 of nanocomposite	free vibration test and the frequency response function (FRF) Analysis

Table 1. Works on damping capacity of materials

2. Experimental measurement methods for damping capacity

As shown in any vibrations textbook, the parameters describing the vibration response of a single degree of freedom (SDOF) spring-mass-damper system may be used in reporting damping test results (Thomson, 1972). Single degree of freedom damping parameters may be estimated by curve fitting to the measured response of material specimens in either free vibration or forced vibration if a single mode can be isolated for the analysis. Approximate

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relationships between the loss factor from complex modulus notation and these SDOF damping parameters exist for lightly damped systems, (Soovere & Drake, 1985) and such relationships will be used frequently in the following subsections.

2.1 Free vibration methods

Observations of the free vibration response of a damped system are often used to characterize the damping in the system. If the specimen is released from some initial static displacement or if a steady-state forcing function is suddenly removed, the resulting free vibration response (Fig. 1a) may be analyzed using the logarithmic decrement, a SDOF damping parameter. The logarithmic decrement is given in Eq. (1)

$$\Delta = \frac{1}{n} \ln \frac{x_0}{x_n} \tag{1}$$

Where x_0 and x_n are amplitudes measured n cycles apart. Eq. (2) is based on the assumption of viscous damping, but for small damping, the loss factor from complex modulus notation may be approximated by Eq. (2) (Soovere & Drake, 1985).

$$Q^{-1} = \frac{\Delta}{\pi} \tag{2}$$

Commonly used modes of testing include torsional pendulum oscillation, and flexural vibration of beams or reeds. Errors may result if more than one mode of vibration is significant in the free vibration response, or if the data are taken at large amplitudes where air damping is present.



Fig. 1. (a) Free vibration decay curve (b) stress-strain hysteresis loop (c) typical frequency response curve

2.2 Forced vibration methods

Forced vibration techniques are often more useful than free vibration techniques when control of amplitude and frequency is desired. Excitation may be sinusoidal, random, or impulsive, and response may be analyzed in either the time domain or the frequency domain.

The simplest forced vibration technique involves the measurement of uniaxial hysteresis loops during low-frequency sinusoidal oscillation of a tensile specimen in a servohydraulic mechanical testing machine. The elliptical hysteresis loops are the Lissajous patterns formed by plotting the sinusoidally varying load (or stress) versus the corresponding strain (Fig. 1b). The energy dissipation ability of the composite material is evaluated by the ratio of the dissipated work by the material (ΔW) to the maximum of elastic energy stored in the cyclic loading process (W), and we use ψ to represent the ratio in Eq. (3) and the loss factor (Q-1) can be calculated from Eq. (4).

$$\psi = \frac{\Delta W}{W} \tag{3}$$

and

$$Q^{-1} = \frac{\psi}{2\pi} \tag{4}$$

With the forced vibration techniques discussed above, data are obtained at the frequency of oscillation of the exciter in the testing machine, which may or may not be a resonant frequency of the specimen. If the forcing frequency is tuned to a resonant frequency of the specimen, the relationship between the input and the response takes on a special form--this is the basis of the so-called resonant dwell method (Granick & Stem, 1965).

By varying the forcing frequency, the so-called frequency response curve (or response spectrum) for the specimen can be swept out in the frequency domain, as shown in Fig. 1c. The peaks in the curve represent resonant frequencies, and SDOF curve fitting techniques such as the half-power bandwidth can be used at these frequencies (Thomson, 1972, Soovere & Drake, 1985). The loss factor here is equal to:

$$Q^{-1} = \frac{\omega_2 - \omega_1}{\omega_n} \tag{5}$$

Where 1/Q is the damping factor and ωn is the peak frequency in the response curves (natural frequency). Parameters $\omega 1$ and $\omega 2$ are referred to as half-power points which are measured at $1/\sqrt{2}$ of peak amplitude.

3. Material preparation and characterization

Al2024 is one of the most widely used Al alloys in aerospace and automobile industries due to their high strength and specific stiffness. To prepare nanostructured Al2024 matrix, Al-4.1 wt.%; Cu-1.9 wt.%; Mg-0.5%Si (Al2024) prealloyed powder was milled in a planetary ball mill (Fritsch P7 type) under argon atmosphere. The milling media consisted of five 20mm diameter balls confined in a 120 ml volume vial. Ball milling was carried out with ball-powder mass ratio of 10:1 and rotation speed of 500 rpm for 30h. 0.5 wt.%. Stearic acid [CH3(CH2)16COOH] was used as process control agent (PCA). Scanning electron

microscopy (SEM-Philips XL30) was used in order to evaluate the morphology changes of Al2024 powder particles through the ball milling process for 30h.

Multi-wall carbon nanotubes (MWCNTs) (provided by Research Institute of Petroleum Industry) were produced using catalytic chemical vapor deposition (CCVD) technique with purity of ~90%. To eliminate the catalyst particles and to disperse MWCNTs, they were immersed in concentrated nitric acid for 12h. MWCNTs were then washed with distilled water and dried at 120°C. MWCNTs sample were characterized by transmission electronic microscope (TEM) (Philips CM12). After that, MWCNTs were added to the ethanol and dispersed using an ultrasonic shaker for 1h in order to maintain uniform distribution. Then, as-milled Al2024 powders were added to the MWCNTs-ethanol solution and the mixture was dispersed using ultrasonic shaker for another 30min. Subsequently, the mixed powders were dried at 120°C in vacuum (~10-2Pa). In order to improve the dispersion of MWCNTs in the nanocomposite powders, ball milling was executed on nanocomposite powders for 4h. In this study, 1, 3 and 5 volume percent of MWCNTs were mixed with 30milled-Al2024 powders. Morphology of nanocomposite powder particles was then examined by SEM.

Final Al2024-MWCNT nanocomposite powders were compacted at 500°C under 250MPa in a uniaxial die and then cooled in air, in order to produce disks with the size of ø50×10mm. The duration of hot pressing was 30 min.

The XRD patterns of as-received Al2024 powders, 30h-milled Al2024 powders and consolidated Al2024-MWCNTs nanocomposite samples were recorded using a Philips diffractometer with Cu Ka radiation (λ =0.15406 nm). The Al grain size in as-milled Al2024 and consolidated Al2024-3vol% MWCNTs samples were estimated from broadening of XRD peaks using Williamson-Hall formula (Williamson & Hall, 1953). Hardness tests were conducted on bulk nanocomposites at a load of 10 kg. The Archimedes technique was used to measure the bulk density of consolidated samples.



Fig. 2. a) As-received Al2024 powder b) 30h-milled Al2024 powder morphology

As-received Al2024 powder particles (see Fig. 2a) were irregular in shape and had nonuniform size ranging from 50 to 300 μ m. According to Fig. 1b, after 30h most powder particles were equiaxed with an average size of ~10 μ m. This decrease in powder particle size is a consequent of stearic acid which diminishes cold welding of powders as well as work hardening effects of Al2024 powders during milling (Jafari et al., 2009).

Fig. 3a shows a TEM image of the purified carbon nanotubes. According to Fig. 3a, it can be found that the MWCNTs have outer diameters of 30 to 40nm and large aspect ratio. Also, it is evident that most MWCNTs enwind with each other, which apparently has a negative effect on dispersing them in the composites. In order to improve the dispersion of MWCNTs in the matrix, the Al2024-MWCNTs nanocomposite powders were mechanically milled for 4h. The SEM image of the nanocomposote powder after milling is shown in Fig. 3b. It is evident that the MWCNTs have been shortened so that the length of most of them has become less than 1µm.



Fig. 3. a) TEM image of purified MWCNTs b) SEM micrograph of 4h-milled Al2024-3%vol MWCNT nanocomposite powders

The XRD patterns of as-received Al2024 powders, 30h-milled Al2024 powders and consolidated Al2024-MWCNTs nanocomposite samples are demonstrated in Fig. 4.



Fig. 4. XRD patterns of as-received Al2024 powders, 30h-milled Al2024 powders and bulk Al2024-3vol%MWCNTs nanocomposite

According to Fig. 4, the structure of as-received powder includes CuAl2 and CuMgAl2 intermetallic compounds. After 30h of ball milling, the intermetallic peaks completely disappeared on XRD patterns owing to the dissolution of CuAl2 and CuMgAl2 intermetallic compounds in Al lattice as well as grain boundaries (Jafari et al., 2009). It can also be assumed that these intermetallic compounds are dispersed into the Al as ultrafine isolated particles which are virtually undetectable by XRD (Tavoosi et al., 2008).

The Al grain size of 30h-milled Al2024 was estimated from broadening of XRD peaks using Williamson-Hall formula (Williamson & Hall, 1953). Due to the mechanical deformation introduced into the powders, Al grains refine so that after 30h of ball milling, Al grain size reaches a value of ~30nm.

XRD pattern of hot-pressed Al2024-3vol%MWCNT includes MWCNT (002) XRD peak appeared at 26.2° in the 2è value, indicating the presence of MWCNTs in the compound. Several peaks of CuAl2 intermetallic compound can be found in nanocomposite XRD pattern. The Al grain size in bulk Al2024-MWCNT was estimated ~42nm, using Williamson-Hall formula (Williamson & Hall, 1953).

4. Modal testing and analysis

The damping factor of the specimen was determined by use of modal testing (DTA, 1993, 2000; Ewins, 2001). The measurement principle consists of recording the free vibrations of the specimen excited by tapping it with an appropriate hammer, as shown in Fig. 5. The amplitude decay as a function of time and the vibration modes were detected by an acquisition data system from B&K Company and recorded using ICATS software (ICATS, 2003) and also by analytical relations.

The test specimen was located on soft foam and tested in a free-free condition. The experimental data were obtained via hammer testing using a B&K Pulse analyzer connected to a PC. One B&K piezoelectric accelerometer (Endevco. 2222c) was attached to the structure by using wax to measure the amplitude decay of the response (Fig. 5). The test parameters were: analyses range of 0-20,000 Hz; acquisition time of 320 ms; rectangular observation window and frequency resolution of 3.125 Hz. Following the testing procedure, two types of curves were obtained: damping free vibration and frequency response function profiles.



Fig. 5. The experimental set-up for modal testing of the specimen

The vibration test gives the free vibration damping decay and the frequency response function (FRF), simultaneously as a result. Considering a linear system of a single degree of

freedom, the FRF response is the decomposition of the natural frequencies of a structure or specimen, which corresponds to a typical fingerprint identity of the vibration modes. The number of vibration peak frequencies (vibration modes) and the shape of the FRF response are a direct result of the material damping.

In the second stage, the experimental FRF data were analyzed using a global multi-FRF analysis method and the results were also checked using available analytical relations. The global multi-FRF technique is based on a complex singular value decomposition of a system matrix expressed in terms of measured FRFs, and then on a complex eigensolution which extracts the required modal properties (Imregun & Ewins, 1995; ICATS, 2003). The data were analyzed by applying 3 runs on each FRF. Typical measured FRF is plotted in Fig. 6.

5. Results and discussion

The values of hardness and bulk density of Al2024 containing 1, 3 and 5vol% MWCNTs are summarized in Table 2.

Considering the data given in Table 2, it can be concluded that with small amounts of MWCNTs addition (less than 3vol. %), the relative density of the composites remains at approximately identical value of ~98%, mainly due to the uniform dispersion of MWCNTs within the Al2024 particles. Consequently, hardness of the composites increases with increasing MWCNTs content. However, large amounts of MWCNTs (~5vol. %) reduce the relative density and hardness of the composites, since MWCNTs tend to tangle together which results in preventing the appropriate densification of the specimens (Deng et al., 2007b).

Material	Relative density (Standard deviation of 0.5%)	Hardness (HV)
Al2024-1vol%MWCNT	98	220±5
Al2024-3vol%MWCNT	97.5	238±4
Al2024-5vol%MWCNT	93.5	195±6

Table 2. Hardness and bulk density values of Al2024-MWCNTs nanocomposites



Fig. 6. Measured frequency response function from excitation of the specimens

The damping capacity was also measured and the results of FRF test are presented in Fig 6. Natural frequency and damping factor are tabulated in Table 3. It comes out true that the natural frequency decreases as the volume percent of MWCNTs reinforcement increases. For damping factor, the trend is the same as hardness value to some extent. In other words, the damping factor increases as the MWCNTs volume percent increase from 1vol. % to 3vol. %. But further increase to 5vol. % causes reduction in damping factor. This phenomenon can be explained in the following way that the MWCNTs reinforcement causes increase in damping capacity but in 5vol. % specimen the cavity content play a more important role and cause reduction in damping factor.

FRF	Natural Frequency (HZ)	Damping factor (Eq. 20)	Damping factor ICATS (LINE FIT TECHNIQUE)
(1% vol CNT)	7302	0.031	.035
(3% vol CNT)	6268	0.052	0.057
(5% vol CNT)	5464	0.0105	.012

Table 3. Natural frequency and damping factor of Al2024-MWCNTs nanocomposites

6. Conclusion

Using a free vibration damping set up, the damping capacity of MWCNTs reinforced metal matrix nanocomposites was measured. It was observed that the damping capacity increases by increasing the vol% of the reinforcement. But as an undesirable feature of production process, increasing the vol% of reinforcement to 5 vol% causes a relatively large amount of porosity in the material which reduces the damping capacity.

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Thermal Conductivity Improvement of PEEK/ZrO₂ Coated MWCNT Nanocomposites

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1. Introduction

Since the landmark paper on carbon nanotubes (CNTs) by Iijima in 1991[1], carbon nanotubes have been an attractive materials for fundamental research studies and become one of the most important materials in the 21st century technology. Several applications were proposed for carbon nanotubes many of which are concerned with conductive or high strength composites [2,3], in which the inclusion of carbon nanotubes in a ceramic matrix is expected to produce composites possessing high stiffness and improved mechanical properties compared to the single phase ceramic material [4] and already been used as nano probes, gas storage containers, nanoelectronic devices, sensors, composite reinforcements, and integrated interconnection due to their extraordinary properties [5-8]. Currently, there has been widespread interest in the fabrication of one-dimensional nano scale materials by filling or coating CNT with various kinds of materials including metals (such as zirconium oxide, hafnium oxide, aluminum oxide, and conductive materials such as gold, copper, and platinum), non-metals, carbides, and oxides which possess distinctive chemical [9-13], mechanical, and physical properties [14-16].

Zirconia (ZrO₂), especially in the powder form, is very attractive material applied in a wide variety of technological fields such as catalysts, oxygen sensors, fuel cells, optical devices, and electronic devices [17-20]. Several preparation methods have also been reported on the synthesis of ZrO₂; including chemical vapor deposition, spray pyrolysis, ion sputtering, solgel, and chemical precipitation [21-24]. This mainly results from its excellent properties including thermal, chemical, and mechanical stability as well as unique optical and dielectric properties.

Carbon nanotubes are widely used in composite materials because CNTs have excellent electrical and thermal properties [25-28], because, a change in structure and properties by diameter, bonding structure, rope structure of carbon nanotube. In contrast, the polymers typically $\sim 0.2W/mK$ has low thermal conductivity. But the rapid development of the electronics industry to emit more heat and small electronic components can be used in polymer materials of high thermal conductivity is required. Temperature rises 10 °C has been reported lost half-life of electronic devices. Therefore, effectively it is important to release heat quickly from electronic components. To develop heat emission high polymer, if

we use the high thermal conductivity of carbon nanotube, thermal conductivity of the polymer can be improved.

Poly (ether ether ketone) (PEEK) is a semi-cystalline thermoplastic polymer with superior mechanical properties, thermal stability and chemical inertness for a wide range of commercial and industrial application. To further extent its engineering uses, it is of great relevance to improve the mechanical performance of PEEK by reinforcing it with nanofillers [29].

However, few efforts have been made to investigate the thermal properties of the ceramicbased CNT nanocomposites. Hence, studying the thermal conductivity of ceramic-based nanocomposites comprising CNT is important. So, in this study, we tried to improve the mechanical properties without harming the thermal conductivity of MWCNT in the PEEK matrix, ZrO₂ coated MWCNT has been used. Zirconium dioxide (ZrO₂) coated MWCNT has been prepared by two methods and compared with pristine MWCNT and virgin PEEK composites in terms of thermal properties were compared.

2. Experimental

2.1 Materials

The PEEK [unreinforced Poly (ether ether ketone)] (450G) has been purchased from DICT, Korea. This material is high performance thermoplastic and having melting point around 343 °C. The multi-welled carbon nanotube (MWCNT) prepared by chemical vapor deposition was purchased from ACN Tech. Co., Korea and purity is more than 95%. ZrOCl₂.8H₂O was employed as the precursor for the synthesis of ZrO₂ coating from Sigma-Aldrich, USA. Ethanol was purchased from Duksan Pure Chemicals Co. Ltd, Korea.

2.2 Processing of composites

2.2.1 Making of MWCNT/ZrO₂ composites

Solid ZrOCl₂.8H₂O was first dissolved in 100 ml of distilled water to produce 0.2 mol/L solution under magnetic stirring. Then 30 mg of MWCNT without any pretreatment were added into the aqueous solution. After 30 min ultrasonic vibration, a black suspensions with MWCNT homogeneously dispersed were obtained. The stable aqueous suspension was then long drawn reflux condensed in a thermostatic water bath at the temperature of 100 °C, ensuring the isothermal hydrolyzing of ZrOCl₂. Figure 1 shows the diagram of the hydrolysis process for the nanocomposites. During this hydrolytic process, the suspension was ultrasonicated for 10 min every 24 h to get a good dispersion of MWCNT in the aqueous solution. After approximately 72 h, the black suspension turned to gray. The advantage of hydrolization method is that shapes of formed nanotubes can be controlled by controlling those of isothermal hydrolization time. Some researchers [30] have already shown that if the hydrolyzation time increased with the reaction time, the thickness of the coating will be increased. So, we can control the shape of the nanotubes by controlling the reaction time. For comparison, a conventional chemical precipitation method was also used to prepare MWCNT/ZrO₂ nanocomposites. By ultrasonic vibration, 30 mg of MWCNT were homogeneously dispersed into 0.2 mol/L of ZrOCl₂.8H₂O aqueous solution to acquire the same stable black suspension. Under vigorous stirring, an appropriate amount of NH₄OH was added drop by drop into the above 100 mL suspension. After that the whole mixture was further magnetically stirred for 60 min, a stable well-proportioned MWCNT/ZrO₂ nanocomposites suspension were obtained.



Fig. 1. A diagram of hydrolysis method and chemical precipitation methods for prepared nanocomposites

2.2.2 Making of PEEK/MWCNT composites and PEEK/ZrO₂ coated MWCNT composites

Brabender Plasticoder (Brabender Co.) has been used for preparation of PEEK/MWCNT composites and PEEK/ZrO₂ coated MWCNT composites. The mixing of sample carried out at 350 °C, 60 rpm for 5 min. Sample of four kinds was prepared. The sample having the code name, such as A, B, C and D for virgin EVA composites, PEEK/pristine MWCNT nanocomposites, PEEK/ZrO₂ coated MWCNT by isothermal process and PEEK/ZrO₂ coated MWCNT by chemical process, respectively and has been shown in Table 1.

	Sample Code			
Composition	Α	В	C	D
	All are in wt%			
EVA	100	100	100	100
Pristine MWCNT	-	3	-	-
ZrO ₂ coated MWCNT by isothermal	-	-	3	-
process				
ZrO ₂ coated MWCNT by chemical process	-	-	-	3

Table 1. Compound formulations

2.3 XRD study

X-ray diffraction (XRD) experiment was carried out in D8 Advance, Bruker AXS (Germany) diffractometer with Cu-K α (wavelength of 0.14051 nm) and a monochromator on the diffracted beam. Experiment was performed at 40 kV of accelerating potential, 40 mA current, and a scanning rate of 5°min⁻¹.

2.4 Dynamic mechanical analysis (DMA)

The dynamic mechanical properties of the samples were determined by using DMA Q800 (TA Instrument, Inc., USA) in tension mode. Rectangular film specimens were used for the

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study. Samples were heated from room temperature to 280 °C at a heating rate of 10 °C/min in air atmosphere within impressed a frequency of 1 Hz.

2.5 Thermal conductivity measurement

DSC measurements were carried out using a TA Instruments Q-20 DSC instrument. The samples (≤ 10 mg), sealed under aluminum pans were scanned in the temperature range of 30 to 400 °C. The heating rate is 10 °C min⁻¹ under the nitrogen atmosphere with a flow rate of 40 ml/min.

Heat flow measurement and heat capacity calculation by used DSC after thermal conductivity was calculated. First, equation (1) has been used to calculate the heat capacity (C_p) of the composites.

$$Cp=(q/t)/(dt/t) = q/dt$$
(1)

where q is the heat flow difference between no sample and with sample, dt is the heating rate. Heat capacity (C_p) was calculated at the three temperatures (T_g , T_m , T_c) indicated by DSC and from the equation (2) thermal conductivity (λ) of the composites was calculated.

$$\lambda = (8LC^2) / (C_p md^2 p)$$
⁽²⁾

where L is sample thickness, C is apparent heat capacity (thick sample), C_p is the heat capacity, m is weight of the thick sample, d is sample diameter, p is oscillation period, 80 s [31].

2.6 TGA study

The equipment (Model TGA Q50), manufactured by TA Instrument, was used to test the samples. For TGA measurements, specimens were cut from the vulcanized samples as small pieces (5-10 mg). The specimens were heated from 30 to 650 °C at a constant increase in temperature (10 °C/min), in nitrogen atmosphere and the weight loss determined as a function of temperature.

2.7 AFM study

The atomic force microscopy was carried out using a Multimode SPM operated in AFM mode and manufactured by XE-100 (PSIA, Korea) at frequency 3 Hz and in non-contact mode.

2.8 Scanning electron microscopy (SEM)

The tensile fracture surface of the samples are scanned in a scanning electron microscope (JSM-6380LV of JEOL Co.; Acceleration voltage: 20kV) to study the dispersion of the MWCNTs in PEEK matrix. Samples are sputtered with gold-palladium prior to testing.

3. Results and discussion

XRD study is performed on the samples using WAXD machines. The change of composites crystallinity is measured on a Bruker AXS X-ray diffractrometer (Germany). WAXD is used to observe the effect of pristine and ZrO₂ coated MWNTs content on the microstructure of pristine PEEK. Figure 2 describes the WAXD patterns for pristine PEEK and PEEK/MWNTs nanocomposites. Within a given range of scattering angles, four characteristic diffraction peaks appear at 2θ value of 18.82, 20.89, 22.84 and 28.92° respectively, which correspond to (100), (111), (200) and (211) reflections, respectively, the matrix orthorhombic unit cell [32].

This experiment confirms once again that the rate of crystallization of the matrix is influenced by the MWCNT types. A remarkable change from promotion to retardation is detected as the presence of wrapped MWCNTs. In contrast, no shift in the position of the Bragg reflections is observed, pointing out that all these composites present the same crystalline structure than pure PEEK. Samples incorporating pristine MWCNTs exhibit larger crystals than pure PEEK, whereas those with wrapped MWCNTs present similar or slightly lower crystal sizes. This behavior is also consistent with the results obtained from DSC analysis. This may be due to the better interaction between the MWCNTs and matrix surfaces resulting in improved adhesion between them at the interface which in turn favors the crystal growth mechanism. In the extreme case of the PEEK with ZrO_2 coated MWCNT

It is also noteworthy that inter-planar distance corresponding to every peak position increases in the case of modified PEEK with MWCNTs, which again support the nucleating ability of nanotube into PEEK systems and support the results obtained from DSC study.



Fig. 2. XRD result of sample (A) PEEK. (B) PEEK/pristine MWCNT, (C) PEEK/ZrO₂ coated MWCNT by isothermal process, (D) PEEK/ZrO₂ coated MWCNT by chemical process

One of the major goals of employing ZrO_2 coated MWCNTs is to attain composites with enhanced mechanical properties, which ultimately determine the application of the material strength. The thermo-mechanical behavior of these composites was studied using dynamic mechanical analysis (DMA). Figure 3 shows, as an example, the dynamic mechanical spectra (storage modulus E', loss modulus E'' and tan\delta) as a function of temperature, at the frequency of 1 Hz, for PEEK and PEEK/MWCNT composites. It is evident that the storage modulus of the composites increases progressively with the addition of wrapped MWCNTs at temperatures below the glass transition, pointing out the stiffening effect of these MWCNTs. Therefore, the remarkable modulus enhancement observed in the PEEK/ZrO₂ wrapped MWCNTs composites should be attributed to a more effective load transfer from the matrix to the fillers likely resulting from the improved dispersing ability of the wrapped MWCNTs, combined with a stronger interfacial adhesion PEEK–MWCNT.



Fig. 3. (a) Storage modulus, (b) loss modulus and (c) Tan δ result of sample (A) PEEK. (B) PEEK/pristine MWCNT, (C) PEEK/ZrO₂ coated MWCNT by isothermal process, (D) PEEK/ZrO₂ coated MWCNT by chemical process

On the other hand, our experimental data reveals a substantial drop in the storage modulus of all the samples between 160 and 180 °C, interval which corresponds to the glass transition of the materials. In this range, differences between E' of each composite and the matrix decrease considerably, and become insignificant at higher temperatures. The main reason is

the strong reduction of the load transfer efficiency in these composites as going through the glass transition.

The evolution of tan δ (ratio of the loss to storage modulus) as a function of temperature for PEEK and PEEK/ZrO₂ wrapped MWCNTs composites is shown in Fig. 3c. Several relaxation peaks can be observed: the maximum at lower temperatures (β -relaxation) is associated with local motions of the ketone groups [33], and the most intense peak (a relaxation) corresponds to the T_g. The incorporation of wrapped MWCNTs results in a small reduction of tan δ magnitude (a measure of the damping within the system) over the whole temperature range. With ZrO₂ coated MWCNTs, all relaxation peaks broaden and shift to the higher temperature side. This indicates that wrapped MWCNTs efficiently restrict the mobility of the PEEK chains, thereby increasing the stiffness of the matrix, which is reflected in higher transition temperatures [34].

DSC is performed on PEEK/MWCNT samples using a DSC 300 F3 (NETZSCH, Germany). Heat flow is monitored over the range of 30 to 400 °C with temperature modulation (+/- 0.8 °C every 60 sec) superimposed on a 10 °C/min heating and cooling rate under purge gas (nitrogen at 40 ml/min). The heating scan thermograms of PEEK and PEEK/ZrO₂-MWNT nanocomposites are shown in Figure 4(a). The pristine PEEK samples produce a main melting peak at 340 °C. However, the addition of MWNTs the shoulder posterior to the main melting peak and an increase end point of the peak.

The addition of ZrO_2 coated MWCNTs also results in small variations of the melting temperature (T_m) of the PEEK matrix (Figure 4a), showing similar trends to those observed from the cooling thermograms (Figure 4b). In the case of composites including 3 wt.% ZrO_2 coated MWCNTs dispersed in matrix, T_m increases ~5 °C, whereas for those incorporating 3 wt.% pristine MWCNT, it increases around ~2 °C than pristine PEEK. It is also important to notice that a small change in the specific heat associated to the glass transition of the matrix in the composites can be visualized in the heating thermograms. The incorporation of ZrO_2 coated MWCNTs dispersed in the matrix shift this transition towards higher temperatures this phenomenon has been proved by DMA measurements.

The thermal conductivity of PEEK composites has been measured from the DSC study and is depicted in Table 2. The thermal conductivity of the composites has been measured in three different temperature zones, namely Tg, Tc and Tm. It has been that thermal conductivity also rises progressively with increasing temperature, as shown in Table 2, being the increment in comparison to the pure matrix (0.22 W/mK). Also, it can be seen that composites loaded with ZrO₂ coated MWCNTs present higher values, indicating that the thermal conductivity is also sensitive to the attributes of the filler, presence of defects and content in metal impurities. ZrO₂ coated MWCNTs samples display slightly lower thermal conductivity than pristine MWCNTs composite, since the wrapping hinders the direct contact among the tubes. Taking into account the exceptionally high thermal conductivity of chemically treated ZrO₂ coated MWCNTs (0.43 W/mK), the improvements in thermal conductivity observed in these composites are more than isothermally treated ZrO_2 coated MWCNTs those expected according to the rule of mixtures. The main reason for this behavior is the coating of the Zr on the MWCNTs. While coating the chemical process is so first that all the MWCNTs are not wrapped by the Zr rather than isothermal process which is slow and steady process. We have already discussed about this in our previous literature [35]. Also, this discrepancy could be attributed to the small thermal conductance of the nanotube-polymer interface and the high interfacial thermal resistance between MWCNTs [36], which limit considerably the heat transfer. Also, it will be quite obvious that thermal conductivity will be higher for the pristine MWCNTs rather than coated MWCNTs.



Fig. 4. (a) Endotherm and (b) exotherm result of the composites (A) PEEK. (B) PEEK/pristine MWCNT, (C) PEEK/ZrO₂ coated MWCNT by isothermal process, (D) PEEK/ZrO₂ coated MWCNT by chemical process

Thermogravimetric analysis (TGA Q500, TA Instruments) is carried out to study the thermal stability of each PEEK/MWCNTs nanocomposite from room temperature to 800 °C at a heating rate of 10 °C/min under purge gas (nitrogen at 40 ml/min). Figure 5 shows the TGA thermograms of PEEK with ZrO_2 coated MWCNTs composites. The thermo-degradation of PEEK and PEEK nanocomposites takes place in one step. The onset degradation temperature of PEEK is around 580 °C but with the addition of pristine MWCNTs and ZrO_2 coated MWCNTs the onset degradation temperature increases. This step of the thermal degradation also takes place at a higher temperature side in the presence of MWCNTs. This

Properties		Sample code			
		Α	В	C	D
T _g (°C)		143.66	147.05	154.17	157.55
T _m (°C)		338.14	339.84	338.48	338.48
T _c (°C)		294.10	294.44	294.44	293.08
	Tg	0.0640	0.0630	0.0614	0.0606
C _p (J/g °C)	T _m	0.0081	0.0103	0.0074	0.0081
	T _c	0.0037	0.0184	0.0148	0.0155
Thermal	Tg	0.22	0.23	0.22	0.22
conductivity	T _m	0.23	0.39	0.30	0.37
(W/mK)	Tc	0.27	0.45	0.39	0.43

Table 2. Heat capacity and thermal conductivity of the composites (A) PEEK. (B) PEEK/pristine MWCNT, (C) PEEK/ZrO₂ coated MWCNT by isothermal process, (D) PEEK/ZrO₂ coated MWCNT by chemical process

region is highly dependent on the types of MWCNTs because the mass loss becomes higher with $ZrO_2/MWCNT$ by isothermal hydrolyzing. On the other hand, Figure 5 also suggests that the MWCNT has a good affinity to the PEEK region in the PEEK/MWCNT nanocomposites, indicating that the MWCNT is dominantly dispersed in the PEEK matrix. As the MWCNT region being increases, thermal properties of the PEEK/MWCNT nanocomposites have been enhanced because the MWCNT possesses good thermal properties. This behavior could be explained by the presence of the char formed from PEEK matrix during the degradation step, which is further stabilized through π - π electronic interactions with the coated nanotubes [37].



Fig. 5. TGA result of the composites (A) PEEK. (B) PEEK/pristine MWCNT, (C) PEEK/ZrO₂ coated MWCNT by isothermal process, (D) PEEK/ZrO₂ coated MWCNT by chemical process

In the present study AFM is also used to study the microstructure of fluoroelastomer/MWCNT samples. From the figure it can be observed that the topographical image of PEEK and PEEK/MWCNTs composite are not as clear as has been observed in other nanotube/polymer composites. However, it is generally known that it is not easy to separate the magnetic contrast from other background forces in MFM topography images. But polymer/nanotube composites are two phase materials with two distinct magnetic properties. The nanotubes are paramagnetic or diamagnetic depending upon their orientation whereas the polymer matrix is paramagnetic. Interpretation of an observed image usually relies on the understanding of micromagnetism.



Fig. 6. AFM images of sample (A) PEEK. (B) PEEK/pristine MWCNT, (C) PEEK/ZrO₂ coated MWCNT by isothermal process, (D) PEEK/ZrO₂ coated MWCNT by chemical process

The homogeneous dispersion of the MWCNTs in the polymer matrix is one of the most important features for reinforcing the composites, since any heterogeneity or aggregation could result in structural defects, which would have detrimental effects on the mechanical properties. A Field Emission Scanning Electron Microscopy (FE-SEM) is performed to observe the morphology of the cryo fractured surfaces (fractured by mechanical force) of PEEK/MWCNT nanocomposites. Figure 7a, is can be observed the furrow like structure of the virgin PEEK matrix. In Figure 7b, MWCNTs (which appear as bright spots) are quite agglomerated, forming a highly entangled interconnected structure. In contrast, for all the ZrO₂ coated MWCNT composites analyzed, the nanofillers are found to be randomly and well-dispersed within the matrix by the shear force from melt-blending (Figure 7c and 7d). No MWCNT agglomerations or entanglements were observed in the whole examined areas;

the energy of the shear force process breaks up the aggregates, leading to a fine dispersion of the coated MWCNTs, which results in a large MWCNT-matrix effective contact area. Moreover, no open ring holes or voids were found around the MWCNTs, hinting at the existence of good filler-matrix interfacial adhesion.



Fig. 7. FESEM images of composite (A) PEEK. (B) PEEK/pristine MWCNT, (C) PEEK/ZrO₂ coated MWCNT by isothermal process, (D) PEEK/ZrO₂ coated MWCNT by chemical process

4. Conclusion

The structure, morphology and thermal properties of high performance semicrystalline PEEK/MWCNT composites incorporating two differently coated MWCNTs have been characterized. X-ray diffraction patterns of the ZrO₂ coated MWCNTs dispersed in the polysulfones revealed an effective debundling and disentanglement of the MWCNTs. TGA thermograms demonstrated a remarkable increase in the degradation temperatures of the composites by the incorporation of the ZrO₂ coated MWCNT. Also, it has been found that thermal conductivity of the chemical treated ZrO₂ coated MWCNT is more good than isothermal treated ZrO₂ coated MWCNT. Scanning electron microscopy observations showed that the wrapped MWCNTs were homogenously dispersed in the thermoplastic matrix using a conventional melt-extrusion process.

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Fabrication of Ion-Induced Carbon Nanocomposite Fibres and their Application to Magnetic Force Microscope Probes

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1. Introduction

1-dimensional (1-D) nanocarbon materials, such as carbon nanotubes (CNTs) (lijima, 1991) and carbon nanofibres (CNFs; 1-D nanocarbon without a hollow structure), are quite "hot" in the materials science field, and a variety of applications is now being tackled, such as scanning probe microscope (SPM) tips, field electron emission devices, nanoelectronics devices, capacitors, catalysts supports, hydrogen storage, and so on. For their synthesis, arc discharge (lijima, 1991), laser ablation (Thess et al., 1996), and chemical vapor deposition (CVD) (Pan et al., 1998; Ren et al., 1998; Tanemura et al., 2001) have conventionally been employed. In those methods, however, growth temperatures higher than 500°C are generally required. From a standpoint of an eco-process and for their applications to flexible devices using plastic substrates, however, they should be grown at lower temperatures, ideally at room temperature (RT). In this respect, plasma-enhanced CVD at and below about 120°C has been attempted (Boskovic et al., 2002; Hofmann et al., 2003). In this chapter, we will deal with a new approach to synthesize carbon nanocomposite fibres at room temperature and their applications to scanning force microscope probes.

2. Room-temperature fabrication of ion-induced carbon-based nanofibres

Ion-irradiation to solid surfaces sometimes induces the formation of nano- to micro-sized surface structures, such as ripples, pyramids, conical protrusions and whiskers, even at RT (Auciello & Kelly, 1984; Czanderna et al., 1998). In addition, surface texturing is sometimes enhanced by a simultaneous supply of so-called "seed" materials which are different from the constituent of the target surface during ion irradiation (Wehner, 1985; Tanemura et al., 2004). These imply that ion irradiation must be promising as a basic technique to fabricate nanomaterials or nanostructures at low temperatures. In what follows, based on this strategy, carbon-based nanofibres (pristine and carbon nanocomposite fibres) are fabricated using the ion irradiation method.

2.1 Pristine carbon nanofibres

In 1980s, before the discovery of CNTs, one of the main topics in the materials science was the growth of whiskers which were generally larger in size than CNFs. For the whisker

growth, an ion irradiation onto graphite surfaces was attempted by several groups using normal-incident ion-beams, and following features had been revealed (Floro et al., 1983; Vechten et al., 1987). (1) Whiskers exhibit an initial rapid growth process of "leads" or "fine whiskers" followed by a slower diffusion-fed process (to form whiskers). (2) All of the fine whiskers point in the incidence direction of the ion beam. (3) Whiskers never grow on diamond or glassy carbon surfaces. Because those investigations focused mainly on the whisker growth, the fine whiskers, which corresponds to the present CNFs, have been treated merely as a precursor to ion-induced C-whiskers and paid little attention. For this reason, features of ion-induced CNFs have yet to be fully revealed.

Figure 1(a) shows a typical scanning electron microscope (SEM; JEOL JEM-5600) image of an ion-induced CNF on a glassy carbon surface irradiated with Ar⁺ ions of 3 keV at 55° from the normal to the substrate with a simultaneous supply of Mo at RT (Tanemura et al., 2004b). As seen in Fig. 1(a), a conical protrusion is formed on the surface, and a linear-shaped single CNF, ~50 nm in diameter and ~1 μ m in length, grow on the tip. Both the basal cone and the CNF are pointing in the ion-beam direction. In the ion-irradiation method, CNFs generally grow only on the cone tips, and more than one CNF never grow on the respective cone tips [Fig. 1(a)]. One of the key factors to induce the ion-induced CNF growth is the ion incidence angle (Tanemura et al., 2005a; Yusop et al., 2010). The ion irradiation at normal incidence is not an optimum condition for the CNF growth, and this may be a reason why the whiskers did not grow on the diamond and glassy carbon surfaces in the previous work done using normally incident ions.



Fig. 1. SEM images of (a) isolated and (b) densely distributed CNFs formed on glassy carbon and carbon-coated Si surfaces irradiated with Ar⁺ ions at 55° from the normal to the surface at RT. Inset in (b): Enlarged image. (Tanemura et al., 2004b; Tanemura et al., 2006a.)

For oblique ion irradiation, densely distributed CNFs are fabricated on not only bulk carbon but also carbon coated substrates without any simultaneous metal supply at RT (Tanemura et al., 2005b; Tanemura et al., 2005c). Figure 1(b) shows a typical example of those formed on a carbon-coated Si surface, revealing that ion-irradiated surface is covered with densely distributed CNF-tipped cones. (Tanemura et al., 2006a). The ion-induced CNFs, which were formed on almost all of the cones [inset of Fig. 1(b)], were linear-shaped and aligned in the ion-beam direction. They were 0.3-1 μ m in length, and almost uniform in diameter, ~20 nm, in the growth direction independent of the CNF length. CNF size was independent of the cone size. It should be also mentioned the ion-irradiation method requires no heat supply. This allows us a greater choice of substrates. In fact, densely distributed CNF-tipped cones grow also on carbon coated plastic substrates (Tanemura et al., 2006a; Tan et al., 2006; Sim et al., 2007). Another feature of ion-induced CNFs is that the higher ion-incidence angle (ion irradiation at oblique direction) produces CNFs of smaller diameter (Tanemura et al., 2005a; Yusop et al., 2010).

The formation of ion-induced CNFs are also possible by Ne⁺ and Xe⁺ ions as well as by Ar⁺ ions (Yamaguchi et al., 2008). Figure 2 shows a comparison of CNFs grown on graphite surfaces by Ne⁺, Ar⁺ and Xe⁺ ions of 1000 eV at 45° from the normal to the surface. The formation of ion-induced CNFs was prominent for the irradiation with lighter mass ions. Longer and denser CNFs tended to grow by lighter-mass-ion irradiation, and finer CNFs were formed by heavier-mass-ion irradiation. In an ion-energy range of 450-1000 V, the higher the ion energy, the longer the length of the ion-induced CNFs. It should be mentioned that the surfaces sputtered by Xe⁺ ions at and less than 600 eV were characterized by sparsely distributed cones and any CNF was not formed thereon. Thus, the size and numerical density are controllable by the ion-irradiation parameters.



Fig. 2. Graphite surfaces sputtered with (a) Ne⁺, (b) Ar⁺ and (c) Xe⁺ of 1 keV. Insets: Enlarged SEM images. (Yamaguchi et al., 2008).

Figure 3(a) shows a typical transmission electron microscope (TEM; JEOL JEM-3010) image of a CNF-tipped cone formed on an edge of a graphite foil irradiated by Ar⁺ ions (Takeuchi et al., 2008a). For the TEM observation, the ion-irradiated graphite foil was directly mounted on a TEM sample holder without any post-treatment. The CNF was ~20 nm in diameter and longer than 500 nm in length. No clear boundary between the CNF and the conical tip was recognizable. In addition, no hollow structure was observed in CNFs, suggesting that they were not CNTs but CNFs. Figures 3(b) and 3(c) show the electron diffraction patterns (EDPs) taken at a middle part of the CNF and a stem regions of the cone, respectively. The EDP from the stem region of the cone featured the spotty rings arising

from the graphite lattice [Fig. 3(c)], disclosing that the stem part of the cones maintained the polycrystalline nature of the graphite substrate. An EDP taken at around a cone tip region consisted of diffraction spots associated with graphite and hallow-like rings, and number of the graphite associated spots was reduced compared with the EDP from the stem region, implying that the graphite nature was less prominent at the cone tip. By contrast, only hallow-like rings were observed in the EDP from the CNF, suggesting the amorphous-like or very fine-crystallite structure of the CNF [Fig. 3(b)]. The observed crystallographic features were similar to those observed for CNFs grown on a carbon-coated Ni mesh (Tanemura et al., 2005b). Hofmann et al. also reported that CNTs synthesized by plasma-enhanced CVD at 120°C were low in graphitization quality (Hofmann et al., 2003). Thus, the amorphous-like nature is a feature common to carbon nanomaterials grown at low temperatures.



Fig. 3. Typical TEM image of a pristine CNF formed on a graphite foil. (b) and (c) EDPs from a middle part of the CNF and a stem region of the cone in (a), respectively. (Takeuchi et al., 2008a)

The growth mechanism of ion-induced CNFs is thought to be as follows (Tanemura et al., 2004b; Tanemura et al., 2005b; Tanemura et al., 2005c; Tanemura et al., 2006b): (i) Formation of conical protrusions, (ii) re-deposition of carbon atoms sputter-ejected from the sample surface onto the sidewall of the conical protrusions, and (iii) the surface diffusion of the re-deposited carbon atoms toward the tips during sputtering (Fig. 4). Because the ion irradiations at elevated temperatures, such as 300°C, were favourable for the longer CNF growth on graphite substrates compared with RT fabrication, it is obvious that the surface diffusion plays a decisive role in the growth of ion-induced CNFs (Yusop et al., 2010).

2.2 Carbon nanocomposite fibres

From a viewpoint of applications, carbon-based nanocomposites are fascinating compared with pristine nanocarbon, due to the wider potential application fields, such as an ultra-high density memory media. Thus, the synthesis of CNTs encapsulating ferromagnetic metals



Fig. 4. Growth mechanism of ion induced CNFs.

has been attempted by CVD methods (Bao et al., 2002; Leonhardt et al., 2003; Alexandrou et al., 2004; Schneider et al., 2004; Tyagi et al., 2005; Elías et al., 2005). For their synthesis, however, besides the high growth temperatures required, the metals which could be encapsulated in CNTs are mainly limited to the catalyst used for the CNT growth. By contrast, in the ion irradiation method in principle, various kinds of metals can be incorporated into ion-induced CNFs by a simultaneous supply of metals during Ar⁺-ion irradiation to carbon or carbon coated substrates at low temperatures.

Figure 5 shows SEM images of graphite surfaces sputtered with a simultaneous Ni supply at a supply rate (D) of 6.0, 7.8 and 15 nm/min (Takeuchi et al., 2008a). The surface sputtered with a small Ni supply (D = 6.0 nm/min) was characterized by CNF-tipped cones similar to the graphite surfaces ion-irradiated without Ni supply [Fig 5(a)]. Ni-supplied CNFs, 20 – 50 nm in diameter and 0.3 – 5 µm in length, were similar to the pristine CNFs in size, whereas in their shape they showed a tendency to curve [see inset in Fig 5(a)]. Such a curved structure was more prominent on the surface sputtered with a moderate Ni-supply [D = 7.8 nm/mir; Fig 5(b)], which was covered with slender needle-like protrusions and cones. The Ni-supplied CNFs grown thereon were not so well aligned, and many of them were curved or waved. They were 30 – 50 nm in diameter and 0.5 – 5 µm in length, and some of them were not uniform in diameter in the growth direction. Thus, the morphology of CNFs was much influenced by Ni supply. As seen below, this may be due to the difference in crystalline structure between Ni-supplied and pristine CNFs.

Another important feature seen in Fig. 5(b) is that the needle-like protrusions or cones do not always possess the CNFs on top. The higher the supply rate, the more manifest this feature, as typically revealed for the surface sputtered with a large Ni supply [D = 15 nm/min; Fig 5(c)]. No CNF was formed on the tops, though the surface featured various sizes of conical structures. Thus, the CNF growth was suppressed by the excess Ni supply. As described above, CNFs are thought to grow due to the redeposition of sputter-ejected carbon atoms onto the sidewall of conical protrusions and the excess surface diffusion of the carbon atoms to the tips during Ar⁺ ion irradiation (Tanemura et al., 2004b; Tanemura et al., 2005b; Tanemura et al., 2005c; Tanemura et al., 2006b). Excess Ni atoms simultaneously supplied would reduce the surface diffusion of carbon atoms to suppress the formation of CNFs.

Figure 6 shows a typical TEM image of a Ni-supplied CNF formed on a cone (Takeuchi et al., 2008a). Similar to the pristine CNFs (Tanemura et al., 2005a; Tanemura et al., 2005b), no boundary between the CNF and the cone was recognizable. In addition, no hollow



Fig. 5. SEM images of graphite surfaces sputtered with a simultaneous Ni supply at D = (a) 6.0, (b) 7.8 and (c) 15 nm/min. Insets in (a): Enlarged SEM image. (Takeuchi et al., 2008a)



Fig. 6. (a) Typical TEM image of a Ni-supplied CNF grown on a cone. (b) EDP from the tip region of the Ni- supplied CNF. Inset in (a): enlarged image of the rectangular area in (a). (Takeuchi et al., 2008a)

structure was observed, implying that it is not tubular, but fibrous unfortunately. Figure 6(b) shows an EDP taken at the tip region of the CNF. The EDP consisted of spotty rings arising from Ni (111) or graphite (101) (the 1st inner ring) and Ni (200) (the 2nd inner ring). Thus, the CNF was characterized by the polycrystalline nature, and Ni was surely included in the CNF, namely the Ni-C nanocomposite fibre (Ni-CNF). From a careful TEM analysis

of the Ni-CNF, fine moiré fringes were observed in several regions of the Ni-CNF [inset in Fig. 6(a)]. This suggests a stack of crystallites in the radial direction of the Ni-CNF. In other words, the Ni-CNF is not simply composed of the Ni grains linearly coalesced in Ni-CNF growth direction whose dimension is comparable to the diameter of the Ni-CNF.

Similar morphological and crystallographic features are observed also for Co and Fe supplied CNFs (Wang et al., 2009; Wang et al., 2010a-c). In every case, with increasing the supply rate, the CNFs are suppressed in formation and tend to be curved. The metal-supplied CNFs possess no clear hollow structure, implying that they are not tubular but fibrous. Although Ni, Fe and Co are known to be typical catalysts for the CNT growth in CVD method, coexistence of those metals and C do not induce the formation of tubular structure in the ion-irradiation at room temperature. The process temperature may be too low to form the tubular structure, namely, CNTs. It should be also noted that with decreasing the metal supply rate, both metal content and the crystallinity of incorporated metals in CNFs decrease. As seen in Fig. 7, for example, CNFs formed with Fe supply at lower supply rates were characterized by broader Debye rings in EDP, suggesting that the nanofibres were amorphous-like or fine crystalline in structure (Wang et al., 2010a).



Fig. 7. Typical TEM image and EDP (inset) of an Fe supplied CNF grown on a graphite foiles at D= 2.0 nm/min. (Wang et al., 2010a)

Metal-carbon nanocomposite fibres can be fabricated also on metal substrates by a simultaneous supply of carbon during ion irradiation without pre-coating of a carbon film. Figure 8 shows SEM images of CNFs directly grown on Cu meshes (Zamri et al., 2010). For the carbon supply, the Cu meshes were placed on a graphite plate and both the Cu meshes and the graphite plate were co-sputtered with Ar^+ ions. The carbon plate acted as the C supply for CNFs growth on metal mesh substrates. The sputtered carbon, unfortunately, was not supplied uniformly over the whole sample surface. So, the CNFs were observed only at a limited area on Cu mesh substrates. Similar to the CNFs grown on carbon substrates, only single CNFs grew on the respective cones and no CNF grew without cone bases. The SEM images clearly indicated that the morphology of the CNFs thus grown were highly depends upon sputtering time. On the Cu mesh sputtered for 30 minutes nanoneedles with fibre length of <1 μ m were formed [Fig. 8(a)], while CNFs grown after the irradiation for 45 minutes were ~2.5 μ m in average length [Fig. 8(b)]. By contrast, the Cu

mesh sputtered for 60 min revealed large needles and the density of the CNFs thereon was quite low. The average length of the CNFs was < $1.5 \mu m$. On Mo meshes also, CNFs were observed to form directly (Zamri et al., 2010).



Fig. 8. SEM images of the morphology of Cu meshes after Ar^+ ion bombardment with a simultaneous C supply for (a) 30, (b) 45 and (c) 60 min. (Zamri et al., 2010)

Figure 9(a) shows a typical TEM image of an as-received CNF contacting with a W nanoprobe of counter electrode (Zamri et al., 2010) to measure the electric property of the CNF. The CNF was formed on a Cu mesh by sputtering for 45 min. As shown in the high magnification image [Fig. 9(b)], dark contrast regions dispersed in the whole area of the CNF. So the CNFs formed directly on the Cu mesh seem to be composite nanofibres. Figure 9(c) represents a selected area EDP at the centre of the fibre. The EDP revealed that the CNF is amorphous-like or fine crystalline in nature. In the EDP, however, the Debye ring was too broad to identify the element contained in the fibre. As seen later, the dark and bright contrast regions in Fig. 9(b) might correspond to Cu and C phases, respectively.

For metal-composite CNFs, a control in crystalline structure was to some extent possible by the electron current flow through the fibres. To investigate the structural transformation of this Cu composite CNF by the electron current flow, a low voltage up to 1mV at an incremental step of 0.2 mV was applied to it with a 4.5 k Ω resistor connected in series while observing its crystalline structure at about × 100,000 (Zamri et al., 2010). The experimental time for this current-voltage (I-V) measurement was 130 sec. Just after the I-V measurement was started, a sudden dramatic change in TEM contrast was observed in the composite CNF and no further dramatic change was recognized during the I-V measurement. Figure 10(a) shows a TEM image taken after the I-V measurement. It should be stressed that after the I-V



Fig. 9. TEM images of an as-received CNF formed on a Cu mesh. (a) A bright field image of a CNFs touching to a W nanoprobe, (b) magnified image of the CNF, and (c) the corresponding EDP. (Zamri et al., 2010)

measurement, the morphology of the composite CNF was changed from linear to wavy, and the crystallinity of the composite CNF was also dramatically reconstructed to a nanocarbon encapsulating a nanowire of polycrystalline nature. In addition, the amorphous carbon transformed to graphene layers at the fibre surface [Figure 10(b)]. Small particles were assembling in the middle of the bundles of graphene layers. It should be also noted that the outer layer of the fibre at which the particles were dispersed, the outer layer composed of bundles of very thin graphene layers (< 10 layers) as shown in Figure 10(c). On the other hand, as shown in Figure 10(d), the outer layer parts without particle dispersion possessed very thick (> 80 layers) graphene layers. During the voltage being applied the resistive heating might occur in the composite CNF and hence inducing the transformation of morphological structure and crystallinity of the composite CNF. Unfortunately, it was impossible to measure the actual temperature increase induced by the current flow. However, the current density reached 265 A/cm² even at the current of 30 nA. Taking account of its quite tiny volume, the temperature would increase over the recrystallization temperature of the composite CNF to induce the transformation. The structural change induced by an electron current flow was also observed by TEM for a Pt-CNT system (welding of a CNT to Pt surface) (Asaka et al., 2008)



Fig. 10. TEM images of the CNF shown in Fig. 9 taken after the I-V measurement. (a) A bright field image, (b) lattice image of outer layer of the CNF (bundles of graphene layers), (c) lattice image of dispersed particles in the bundles of graphene layers and (d) lattice image of thick graphene layers formed in the outer layer of the CNF. (Zamri et al., 2010)

3. Nanoprobe application

Ion-induced carbon-based nanofibres cover many of the application fields of CNTs. Among them, their application to SPM probes will be the most promising in the nearest future. In SPM, localized interaction between a SPM tip and a sample surface is measured as a function of the tip (or sample) position to create an image with an atomic resolution. Thus, essential factors for probes affecting the SPM performance are geometrical factors, namely, sharpness in tip radius and aspect ratio. Sophisticated control in specific property, such as chirality of CNTs, is not required for the probe application. In addition, probes perform well independent of a hollow structure of the 1-D nanocarbons. Thus, both CNTs and CNFs are potential candidates for this application. In this chapter, we will deal with the application of the 1-D nanocarbon materials to SPM probes.

3.1 Batch-fabrication of carbon nanofibre probes

Since the development of the scanning tunneling microscope (STM) (Binnig et at., 1982), a variety of probe-based microscopes, such as atomic force microscopes (AFMs) and magnetic force microscope (MFM), has been proposed and widely used in the various fields of semiconductor engineering, surface science, biology and so on. Sharpened metal probes and Si (or SiN) probes are commercially used. In order to achieve higher spatial resolution, the sharper or finer probes are indispensable. Thus, from just after the discovery of CNTs (lijima, 1991), 1-D nanocarbons such as CNTs and CNFs, have been thought as an ideal probe for SPMs, because of their high aspect ratio, nanoscale tip radius of curvature and chemical stability. Typical approaches to fabricate CNT- or CNF-tipped probes include the attachment or the direct growth of 1-D nanocarbons onto probe tips (Dai et al., 1996; Wong et al., 1997; Wong et al., 1998a; Wong et al., 1998b; Nagy et al., 1998; Nishijima et al., 1999; Nakayama et al., 2000). In the attachment methods, although high quality CNTs can be utilized, the attachment is done one-by-one manually or electrophoretically. So, this method is not suitable for the mass production to be used in industrial researches, but usable in laboratory research. On the other hand, the direct growth of a CNT onto an SPM tip by CVD was first demonstrated by Dai, et al (Dai et al., 1996). This CVD method has been expected to have a potential for mass production of CNT probes (Hafner et al., 1999a; Hafner et al., 1999b; Cheung et al., 2000). In fact, E.Yenilmez, et al. demonstrated the waferscale growth of single CNTs onto commercial-type Si cantilever tips by a so-called "surface growth CVD" (Yenilmez et al., 2002). In this method, however, an additional one-by-one post-processing of individual CNTs to tune their length is required for the practical use (Bhushan, 2003). Thus, in spite of the devoted much effort, the large-scale fabrication of practical CNT- or CNF-probes is still quite challenging.

As described above, in the ion irradiation method, ion-induced CNFs grow only on the sharp tips and SPM probes possess the sharp tips originally. In addition, they grow on the whole ion irradiated area. So, a batch fabrication of CNF-tipped probes (CNF probe) should be achievable using a large-scale ion gun.

Figure 11 shows a typical optical microscope image of an array of commercial Si cantilevers (tetragonal-type Si tips; Olympus) and SEM images of a CNF grown thereon using the ionirradiation method (Tanaka et al., 2007). The growth duration (ion-irradiation time) was 9 min. As seen in Figs. 11(c) and 11(d), a linear-shaped single CNF, about 800 nm in length, pointing in the ion-beam direction, grew only on the tip. The CNF was almost uniform in diameter, ~30 nm, along the growth direction. The length of CNF probes was well controllable by the growth time, because the CNFs increased in length with growth time. After the 32 min irradiation, for instance, CNFs were longer than 1.7 µm in length. Independent of the growth time, CNF probes were linear in shape and almost uniform in diameter along the growth direction. Fine CNFs tended to grow for short irradiation duration (< 10 min). Under the optimized growth condition, CNFs were batch-grown uniformly in length with the standard deviation of less than ~10 % (9 chips/batch in this experiment). Needless to say, the batch fabrication system can be readily scaled up by using a larger ion beam source. In fact, wafer-scale fabrication, more than 280 SPM chips in a 4inch wafer, was challenged, and ~80 % of the CNF probes batch-grown were suitable for practical uses as qualified probes. (Kitazawa et al., 2009)



Fig. 11. (a) Optical microscope image of an array of SPM chips used for the batch growth (9 chips/batch). (b) SEM image of the cantilever of encircled area in (a). (c) and (d) Front-view and enlarged side-view SEM images of a typical CNF probe thus batch-grown, respectively. (e) SEM image of a CNF grown in 45°-derection to the cantilever plane. (Tanaka et al., 2007)

One of the most important applications for CNT or CNF probes is the precise analysis of deep trenches. For this application, probes should approach the bottom surface of the trench as perpendicularly as possible, in order to avoid the contact to the side wall of the trench with the probe. Thus, the controllability in the growth direction of CNFs is quite important. Since the ion-induced CNFs grow toward the ion beam direction (Tanemura et al., 2004b; Tanemura et al., 2005a;, Tanemura et al., 2005b; Tanemura et al., 2006b), the growth direction of CNFs is readily controllable by incidence angle of ions, as typically exemplified in Fig. 11(e).

Figure 12(a) shows an SEM image of the villus-like structure to check the performace of the batch fabricated CNF probes, disclosing that the plastic nanocolumns of 50 - 60 nm in diameter and 40 - 50 nm in inter-nanocolumn spacing were densely arrayed (Kitazawa et al., 2009). A CNF probe used in this measurement was 16 nm in diameter, 353 nm in length, and 7.4 deg in growth angle. The probe mounted angle was 12 deg, so that the actual angle of the probe tip was 4.6 deg. For a comparison, AFM observation using a conventional Si probe was also carried out. AFM images obtained using the CNF and the Si probes are shown in Figs. 12(b) and 12(c), respectively, with respective cross-sectional line profiles. The image obtained by the Si probe was distorted as seen in elliptical shapes of respective nanocolumns. By contrast, the AFM image attained by the CNF probe was not distorted, and as also seen in the cross-sectional line profile, side wall structure of nanocolumns was observed more symmetric and abrupt compared with that depicted using the Si probe. The superiority of the CNF probe was confirmed quantitatively by measuring the side-wall angles of 10 nanocolumns randomly selected. For the CNF probe, averaged wall angles of right- and left-sides of the nanocolumns measured 85.5° (2.4° in standard deviation σ) and 80.6° (1.8° in σ), respectively, whereas they were 86.0° (1.5° in σ) and 73.8° (6.0° in σ), respectively, for the Si probe. As is clear from this result, the CNF probe provided a symmetric profile with a less σ value in the distribution of side-wall angles of nanocolumns.



(b) CNF Probe



Fig. 12. (a) SEM image of a densely distributed plastic nanocolumn array and its AFM images obtained by (b) a CNF and (c) a conventional Si probes. (Kitazawa et al., 2009)

From a viewpoint of the practical use, easy handling of probes is also important. In case of CNT probes, for instance, a special care is required for AFM measurements. By contrast, CNF probes can be used as easily as conventional Si probes. This point is quite fascinating for the daily use. Thus, it is believed that the batch-fabricated CNF probes would be quite promising for various application fields.

3.2 Application of carbon nanocomposite fibres to magnetic force microscope (MFM) probes

As seen above, various kinds of metals, such as ferromagnetic metals, can be incorporated into ion-induced CNFs by a simultaneous supply of metals during Ar⁺-ion irradiation (Tanemura et al., 2005a; Tanaka et al., 2007; Wang et al., 2009; Wang et al., 2010a-c). If the metal incorporation is possible also for CNF probes, their magnetic, electrical, mechanical and chemical properties will be readily controllable, and thus their wider range of applications being realized.

Figure 13(a) shows an SEM image of a typical Co-CNF probe batch-fabricated (8 chips/batch) by Ar⁺-ion irradiation with a simultaneous Co supply (Sugita et al., 2009). For

basal cantilevers, commercial Si probes (tetragonal-type Si tips; Olympus) were used. As clearly seen in the SEM image, a single nanofibre grew in the ion-beam direction on the original Si tip. As confirmed by the energy dispersive spectroscopy (EDS) analysis of a tip region of a nanofibre, Co and C were contained in the fibre, and hence proving that the nanofibre was a Co-CNF. Thus, similar to the pristine CNF probes, Co-CNFs probes are producible in a batch process readily.



Fig. 13. (a) SEM image of a typical Co-CNF probe. (b) Typical EDS spectrum attained for a Co-CNF probe. (Sugita et al., 2009)

The Co-CNF probe shown in Fig. 13(a) was 20 nm in diameter and 400 nm in length. It was shorter in length than pristine CNFs fabricated under the identical ion-beam conditions without a Co supply, though their diameter was almost identical with that of pristine CNFs (Tanaka et al., 2007; Kitazawa et al., 2007; Kitazawa et al., 2008). As seen in the previous section, metal supplied CNFs formed on graphite substrates in general decrease in length with increasing the metal supply rate. This is also the case for Co-CNF probes. Co-CNF probes decreased in length almost linearly with an increase in Co supply rate, whereas their diameter was almost independent of the Co supply rate in the range of Co supply rate at which Co-CNFs are successfully formed. It should be emphasized that without thickening diameter remarkably an incorporation of metals into CNFs was readily achievable by the ion-irradiation with a simultaneous metal supply. This point is quite important for the development of the high performance MFM probes. Another possible method to produce nanocarbon based MFM probes is a post-deposition of a metal film onto 1-D nanocarbon probes. This method, however, increases the diameter of the 1-D nanocarbon, resulting in a decrease in the image resolution.

Figure 14 represents images taken in AFM and MFM modes using a Co-CNF probe batch fabricated for a magnetically recorded media (used hard disk) (Sugita et al., 2009). Small surface roughness of the film was observable in the AFM image [Fig. 14(a)], implying that the Co-CNF probe possessed an enough spatial resolution in AFM mode. In the MFM image, clear bright and dark stripes corresponding to magnetic signal patterns were observed. So, the ion-induced Co-CNF probe is applicable also as an MFM probe.

For the better image resolution finer probes are required, and for higher MFM sensitivity larger amount of Co should be included in the Co-CNF probe. As was described in the previous section, however, an excess supply of the metal to CNFs tend to suppress the CNF formation and formed metal supplied CNFs tend to be larger in diameter. So, for the best



Fig. 14. (a) AFM and (b) MFM images observed by a batch-grown Co-CNF probe. (Sugita et al., 2009)

MFM performance, Co content and Co-CNF diameter should be optimized. This is our next subject. In addition, in this ion irradiation method, metal alloys whose ferromagnetic property are stronger than Co can be supplied. MFM performance of such a alloy supplied CNF probes is quite interesting. These experiments are in progress.

4. Conclusions and future prospects

The room-temperature fabrication of carbon-based nanocomposite fibres by the ionirradiation method and their applications to AFM and MFM probes were demonstrated. CNF-based AFM probes have already been released for the commercial uses. For a broader range of industrial researches, their stable production in larger wafer-scale is indispensable. In addition, the importance in the controllability in electrical, mechanical, magnetic and chemical properties of the nanoprobes will be increasing in practical applications, especially in nanotechnology and biotechnology fields. The MFM probe demonstrated here is the first step of these "functionalized probes" based on the composite CNFs. For the development of such advanced nanocarbon based probes, basic researches on the dependence of those properties on the amount of the contained metals in CNFs are necessary. In addition, the control in the crystalline structure of composite CNFs by electron current flow is quite important from viewpoints of both fundamental research and application. The investigations along these lines are now being undertaken.

Besides the probe applications, ion-induced pristine and composite CNFs are applicable to field electron emission devices (Tanemura et al., 2005b; Tanemura et al., 2005c; Tan et al., 2006; Sim et al., 2007; Ghosh et al., 2010; Wang et al., 2009). In addition, by using the ion

irradiation method, ZnO based composite nanoneedles for ultra violet laser emission (Lau et al., 2005; Tanemura et al., 2006c; Yang et al., 2006; Tanemura et al., 2007) and spintronics devices (Herng et al., 2007; Herng et al., 2009) can be fabricated. Furthermore, various kinds of metal- and semiconductor- nanocomposites can be fabricated at low temperature by the ion-irradiation method (Ghosh et al., 2010b; Kutusna et al., 2009; Miyawaki et al, 2008). Thus, the ion-irradiation method is believed to be a new route to fabricate nanocomposite materials at low temperatures.

5. References

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Nano Reinforcements in Surface Coatings and Composite Interphases

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1. Introduction

Nano reinforcements have aroused considerable attentions from both material science and engineering application points of view because of their extraordinary mechanical properties and electronic structures. The use of nanoclays, carbon nanotube networks in surface coatings and composite interphases is leading to rapidly growing unique areas of nanotechnology, especially in integrating mechanical and electrical functionality on the nanoscale. A more comprehensive understanding of the role of nano reinforcements on material surface defect repairing and the realization of functional composite interphase is a significant research focus.

Most solid materials have surface defects. In brittle materials such as glass and ceramics, a fundamental mechanism of failure is the spreading of surface defects. Surface defects of brittle materials cause actual tensile strength much lower than the ultimate theoretical strength. The surface defects normally on the nanoscale providing extra stress at the tip of the cracks can lead to stress-corrosion cracking at low stress level. Generally, polymer coatings are always applied to various fibres to protect them from mechanical damage during handling. Such coatings also act as a diffusion barrier to moisture reaching the fibre surface from the surrounding environment. Healing nanoscale surface flaws and enhance materials' lifetime by coating, therefore, are important for many traditional materials for wide use in aggressive environments. The mechanical 'healing' effect was viewed as a disappearance of the severe surface flaws because of an increase of the crack tip radius, the flaw filled by coatings being either elliptical than sharp. Reinforcement with nanomaterials in coatings is a topic of significant current interest. The molecular dynamics simulations show that the stress concentration at the notch tip is significantly reduced due to the presence of the nanoparticles (Tyagi et al., 2004). These results point to a simple means of fabricating systems that can self-heal, where nanoparticles dispersed in a polymer matrix can migrate to a crack generated at the interface between the polymer and a glassy layer (Gupta et al., 2006). Fundamentally, optimised mechanical structure and nanostructured surface are motivated by the grace and efficiency of natural materials, in a biomimetics approach. It is evolved in these materials, as shown in Fig. 1 (left), that multiscale structures (i.e. bones) and skin coverings with flexible multilayer of overlapping tough scales (vertebrates, i.e. fishes) provide a protective layer against physical/chemical attack. The nanometer size of mineral particles, composed of insoluble protein keratin and minerals, ensures optimum strength and maximum tolerance of flaws (Gao et al., 2003). As the structural size shrinks to the nanometer scale, there is a transition of fracture mechanism from the classical Griffith linear elastic fracture mechanics (LEFM) to one of homogeneous failure with no stress concentration at the crack tip and the structure becomes insensitive to pre-existing flaw (Gao & Ji, 2003). The surface free energy becomes more dominant and the material strength is limited by theoretical strength of solid. The surface defect-free and high purity carbon nanotubes have exceptional high Young's modulus and tensile strength. However, an effective utilization of their mechanical properties in composites is a long standing problem. To date, the highest strength and Young's modulus reported in the literature are relatively disappointing: $1.8 \sim 3.2$ GPa and ~ 40 GPa, respectively, for aligned nanotube composite bundles with very high volume loading of nanotubes (60 wt%), which are a factor of ten below those of the component individual nanotubes (Vigolo et al., 2000, 2002). Our recent work applied a 'surface defects healed by super-materials' approach to glass fibres since glass fibres are most widely used traditional reinforcements in composites globally (Gao et al., 2007). Using nanotubes in coatings to heal common continuous glass fibre, strengthening as much as 60% is achieved because surface coatings can efficiently protect the fibre surface against alkali/acid/moisture and thus improve fibre's mechanical properties. The mechanical properties of the healed glass fibres are equal and even higher than the corresponding values of aforementioned high volume concentration bundled nanotubes.



Fig. 1. Natural strategy of mechanical reinforcement and environmental resistance by multiscale fibres and overlapping tough scales (left). Applications of nanostructed coatings with nanotube/layered silicate polymer network on glass fibre surface to enhance healing flaw effect and corrosion resistance (right). The inserts show polymer/multi-walled carbon nanotubes (MWCNT) network by SEM and individual surface functionalized nanotube structure by TEM.

Another fundamental feature of glass fibre is electrical insulating. The development of novel glass fibre reinforced plastics (GFRPs) with electrical conductivity has opened up new opportunities in which unique functionality can be added to existing material systems for a broad range of applications, including electrostatic dissipation, electric field shielding, damage detecting, etc. As pilot approach, the electrical conductivity of GFRPs has been achieved by either adding conductive particles, such as carbon blacks and carbon nanotubes (CNTs) in polymer matrix, or composite surface treated with antistatic or metallic coatings (Thostenson et al., 2006, 2008, Böger et al., 2008). As outstanding multifunctional sensing materials, recently, CNTs have stimulated the development of various conductive nanotube/polymer composites with sensitive features to piezoresistivity, temperature and moisture (Baughman et al., 2002; Bekyarova et al., 2007; Veedu et al., 2006; Dzenis, 2008). The piezoresistivity of carbon nanotubes has been known for several years, i.e., nanotube electrical resistance changing by mechanical stress (Tombler et al., 2000). The GFRPs with carbon blacks and MWCNTs in polymer matrix with health monitoring functionality have recently been successfully developed to monitor damage initiation and evolution. Thostenson and Chou processed GFRPs with embedded CNTs in epoxy matrix to evaluate the onset and evaluation of damage (Thostenson et al., 2006, 2008). One outstanding challenge is to fabricate in-situ sensing composite materials at micrometer scale, especially at interphase of composites (Gao et al., 2010; Zhang et al., 2010), being capable of detecting stress/strain, temperature and humidity with high sensitivity.

Herein, we describe a method that introduces electrical conductivity to glass fibre surface by depositing MWCNT networks, and in turn, specifically forming an interconnected MWCNTs-rich interphase within glass fibre reinforced epoxy composites, showing the potential to realize multi-scale fibre reinforced composites with multifunctional properties. Aimed at multifunctional applications, we performed in-situ DC electrical resistance measurements of the single MWCNTs-glass fibre and 'unidirectional' MWCNTs-glass fibre reinforced epoxy composites at different temperatures, relative humidities (RH), fibre orientations and tensile strains underwent uniaxial tensile or cyclic loading, respectively. The surface morphology of the fibres, interphase properties and the glass transition temperature of composites were studied by ultra high resolution field emission scanning electron microscopy (FE-SEM) and atomic force microscopy (AFM), electric force microscopy (EFM), nanoindentation and differential scanning calorimetry (DSC), respectively. Our approach will help to validate and improve the technique of in-situ monitoring/sensing in advanced nanocomposites, implying highly sensitive to the fracture of the load-carrying fibres and the development of cracks in the fibre/polymer matrix interphases, where the microscale damage is usually initiated.

2. Experimental

2.1 Glass fibre coated by polymers and MWCNTs or clay

The control alkali-resistant glass (ARG) fibres utilized in this work were made at our institute with diameters of 17 μ m. During the continuous spinning process, the ARG fibres were in-situ sized by an alkali-resistant sizing consisting of silane coupling agent, γ -aminopropyl-triethoxysilane, in conjunction with film formers and nanoparticles in the aqueous sizing, namely S1. The 0.2 wt% surface functionalized MWCNTs (IFW, Germany) are dispersed in the epoxy film former based sizing. We applied surface coatings to the control ARG using either two kinds of styrene-butadiene copolymers with different T_g

values (C1) or a commercial self-crosslinking styrene-butadiene copolymers (C2). Similarly, E-glass fibres with diameters of 20~23 µm were also coated with less than 0.5 wt% nanotubes in the coatings. The organo-clay particles (Nanofil 15, Süd-Chemie AG, Moosburg, Germany) in maleic anhydride grafted polypropylene with a size of about 60 to 130 nm are dispersed in the obtained solution. A quaternary ammonium surfactant and a non-ionic surface active agent were added to the dispersion for homogeneous distribution of the constituents with or without 1 wt% nanoclay. This method benefits from its ambient temperature treatment and environmentally friendly deposition, in addition to chemical versatility. The total weight gain due to the coatings is 5.3 wt% measured by pyrolysis (600 °C, 60 min) of the coated fibres. We extracted the fibres in selected highly concentrated aqueous alkaline solution (5 wt % NaOH, pH of 14) at 20 °C for seven days, which is the most aggressive and corrosive condition to the fibre surface.

2.2 Glass fibre coated by MWCNTs and glass fibre/epoxy composites

Briefly, various aqueous dispersions with the pH value of 5~6 and 0.5 wt% carboxyl functionalized MWCNTs (NC-3101, Nanocyl S.A., Belgium) were utilized for ensuring more homogenous distribution of CNTs on glass fibre surfaces. The dispersion aids are non-ionic, cationic or anionic surfactants, namely Igepal CO970 (shown schematically in Fig. 2(a)), Arquad S-50, and sodium dodecyl sulfate (SDS), respectively. The glass fibres were dipped into MWCNTs dispersion for 15 min and dried in a vacuum oven for 8 h. A commercial DGEBA-based epoxy with amine hardener (EPR L20, EPH 960, Hexion Speciality Chemicals GmbH, Germany) in a weight ratio of 100:34 was used as matrix and the single glass fibre and unidirectional MWCNTs-glass fibre reinforced epoxy composites over a very wide range of glass fibre volume fractions from 4×10-3 % to 50 % were cured at identical conditions (80 °C, 6 h), where no additional CNTs were added to the matrix. For electrophoretic deposition (EPD) coating, silane coupling agent 3-Glycidyloxypropyltrimethoxysilane (Dynasylan® Glymo, Evonik Degussa Corporation, Germany) was added into CNT dispersion to introduce functional groups onto fibre surface and to improve the interfacial shear strength. The concentration of MWCNTs was as small as 0.05 wt%. We used two parallel copper plates with rectangular-shape as cathode and anode. According to streaming potential results, the dispersed MWCNTs and the hydrolyzed Glymo showed negative charge and migrated towards the positive electrode, the anode was used as deposition electrode, glass fibres were fixed on a thin plastic frame, and then the frame was mounted on the anode, which is schematically shown in Fig. 2(b). EPD experiments were carried out at constant voltages, deposition time of 10 min, and an electrode distance of 8 mm. The coated samples were dried at 40°C in a vacuum oven for 8 h. Due to their very small size and well-dispersed state, the carbon nanotubes were able to penetrate into the spaces between the fibres and coagulate on the whole surface of fibre.

2.3 Characterisation

The MWCNTs-glass fibre surface and composite interphase properties were studied using ultra high resolution field emission scanning electron microscopy (FE-SEM Ultra 55, Carl Zeiss SMT AG, Germany) and AFM (a Digital Instruments D3100, USA). AFM modes of tapping, LiftMode electric force microscopy (EFM) and nanoindentation were performed to obtain topography morphological, electric force images and nanomechanical stiffness, respectively. To assure good topography imaging resolution and nanometer scale indents,



Fig. 2. Schematic illustrations of (a) MWCNTs dispersion process in water with surfactant and (b) deposition of MWCNTs onto insulative glass fibre surface by the electrophoretic deposition cell.

the ultra-sharp cantilever (NSC15-F/5, MikroMasch, Estonia) has a radius of ~10 nm, a normal spring constant of 40.9 N/m and modulus of 160 GPa. An electrical field can be induced by applying a voltage of 12 V between an ultra sharp conductive AFM tip (NSC-14/W2C/15, MikroMasch, Estonia) and the nanotube rich interphase, where the tip interacts with the interphase through long-range Coulomb forces at a constant distance of 50 nm. We detected the phase shifts to create EFM images, arising from the interactions changing the oscillation phase of the AFM cantilever, where attractive forces make the cantilever effectively "softer" reducing the cantilever resonant frequency, and conversely repulsive forces make the cantilever effectively "stiffer" increasing the resonant frequency. To ensure a low surface roughness across the interphase, the specimens were polished perpendicularly to the fibre axis with a SiO₂/Al₂O₃ suspension down to an average grain size of 60 nm. In addition, the T_g was measured for the composite sample with fibre volume fraction of 40% by the modulated DSC (Q2000 MDSC, TA Instruments, USA) at the rate of temperature change of 3 K/min.

The technique applied to operate and measure the electrical property of a single MWCNTsglass fibre has been realized, using one fibre bridging two Cu electrodes on epoxy substrate with small gap distances of 0.3, 1.0, and 2.2 mm, respectively. Without using conductive silver paste, the fibre was assembled carefully along a narrow channel ditch on the relatively soft Cu electrodes, which was prefabricated by surface indentation using the same kind of glass fibre. In this configuration a large amount of MWCNTs on the fibre surface was forced to attach to the electrodes under compression. Besides, the surface forces, van der Waals, and capillary forces are enough to establish a sufficiently intimate electrical and mechanical contact between the nanotubes and the electrodes [45]. Approximately ten fibre specimens for each condition were measured. Two-probe setup with a Keithley 2000 multimeter and a DC power supply (ELV PS 7020) was used to obtain the I-V curves. Four-point conductivity measurements were carried out to monitor the DC electrical resistance using a Keithley 2000 multimeter and two-point conductivity was also carried out with LCR-digital multimeter (VC-4095) for the resistance value higher than 100 M Ω of single MWCNTs-glass fibre. We further performed in-situ electrical resistance measurements of the single MWCNTs-glass fibre at different tensile strains, temperatures, relative humidities (RH). The tensile strength of single fibre was measured using the Favigraph semiautomatic fibre tensile tester (Textechno, Germany) equipped with a 1 N load cell, according to DIN EN ISO 5079 and DIN 53835-2, respectively. To investigate the piezoresistive effect, the electrical resistance was recorded as the single glass fibre underwent uniaxial tensile or cyclic loading. The tests have gauge length of 20 mm and the cross head velocity of 0.2 mm/min for both loading and unloading with strain amplitude of 2%. To ensure good electrical contact, gold deposition with thickness of about 60 nm was sputtered to two ends of single MWCNTsglass fibre except of the middle part of fibre with length of 2 mm for the measurement. The specimen was in turn clamped between two plates coated with conductive silver paste (Acheson Silver DAG 1415M) serving as electrodes. Simultaneous resistance, strain, and load measurements were integrated with time scale in a customized data acquisition package TestPoint 2.0. In order to further detect composite piezoresistive effect, mechanical tensile/compression strains were performed using a self-made screw-driven tensile stage and simultaneous resistance was recorded at each strain step. The experiments of the resistance changing with the temperature were carried out in a hot-stage (Linkam LTS350 Heating/Freezing, UK) from -150 °C to 180 °C with a heating rate of 1 K/min in a nitrogen atmosphere. We prepared unidirectional MWCNTs-glass fibre/epoxy composites over a very wide range of volume fractions from 4×10^{-3} vol% to 50 vol%, including dog-bone shaped samples (20×1×1.8 mm³) and rectangular-shaped samples (20×7×1.8 mm³) for electrical testing. The surface for electrodes was mechanically polished with 2400 grade silicon carbide grinding paper followed by sputter coating of gold layer with thickness of about 60 nm.

3. Results and discussion

3.1 Nano reinforcements in fibre surface coatings: mechanical properties

We first investigated the tensile performance of the single fibre with nano reinforcements in surface coatings (Fig. 3). In comparison with unsized samples, we observed a significant improvement of 70% of tensile strength for nanostructured glass fibre with nanotubes. The fibre strength also increased up to 40 % and 25 % for sized fibre and sized fibre with 1 wt% loading of organoclay in the sizing, respectively. The fibre fracture behaviour is strongly affected by the variation of sizing properties because the critical flaws which limit the strength of fibres are located at the surface. Additionally, the effects of alkaline attacks on the average fibre strength are also compared in Fig. 3. It is evident that sample of clay

coatings would not yield a significant strength reduction upon alkali treatment. Therefore, the durability and alkali-resistance are also improved, particularly the fibre with organoclay coatings. Overall, the coated fibres have higher strength values than the control one after alkaline corrosion, reflecting the improved environmental durability for fibres with nanostructured coatings.



Fig. 3. Effect of the nanostructed coatings with low fraction of nano-reinforcements on the tensile strength of ARG before and after alkaline treatment in 5 wt% NaOH aqueous solution for seven days in an ambient environment. Error bars represent standard deviations for the estimate of the mean strength of fifty samples.



Fig. 4. A sketch of a coated fibre with a surface flaw. The fibre is loaded in tensile stress σ and the circumferential surface flaw of length *a* serves as an initial crack. The fibre diameter and coating thickness are given by *d* and *L*, respectively, where *a* and *L* are much less than *d*.

Potential mechanisms include the contributions of different factors for the mechanical property improvement by reducing the fibre surface flaw formation and crack growth. Note that the polymer coatings have Young's moduli that are typically several orders of magnitude lower than the glass fibre, and therefore do not bear a significant portion of the mechanical load. Although the polymer coatings do not increase strength, they have the important function of protecting the glass surface from abrasion and chemical damage, which in turn would degrade glass fibre strength. The coating layer with organosilicate plates could prevent moisture/alkali contact and reaction with glass lattice at a crack tip (stress corrosion). The acidic groups of coating molecular interact with or absorb free cations and anions of environment leading to a slow-down of the corrosion process. Secondly, stress-redistribution and crack stopping mechanisms by coatings and nanotube's 'bridging' effect and interface debonding/plastic deformation around crack tip. The mechanical 'healing' effect was viewed as a disappearance of the severe surface flaws because of an increase of the crack tip radius, the flaw filled by coatings being either elliptical than sharp. Thirdly, compressive stress on fibre surface might prevent crack opening/propagation by the shrinkage of polymer due to solidification. Because of the compression closing surface flaw, the strengthening can be increased by increasing the magnitude of the compressive stress.

To simplify the complex phenomena, we developed a simple mechanical model based on Griffith fracture mechanics to roughly estimate the strength of coated fibre. Consider a smoothly coated fibre loaded in tension and having a thin circumferential crack (Fig. 4). When the crack appears, the strain energy is released in a material volume adjacent to the crack. Assume that this volume is comprised by a conical ring whose generating lines are shown by broken lines and heights are proportional to the crack length. The present assumption is arbitrary and significant analogy to the original Griffith strain energy analysis for an elliptical, sharp crack embedded in a flat, brittle sheet. Accordingly, the energy is consumed by formation of new surfaces and deformation of coatings because of an elastic constraint. According to the energy balance, the coated fibre strength, σ_{j} can be expressed as

$$\sigma_f > \overline{\sigma}_f = \sqrt{\frac{2\gamma E_f}{(\beta a^* - \frac{L(1 + L/d)E_c}{E_f})}}$$
(1)

where γ is fracture surface energy and β (=1-2*a**/3*d*) is a constant coefficient of proportionality which is very close to one since an apparent crack length *a** is much less than fibre diameter *d*. We used the apparent crack length *a** instead of *a* to take into account geometrical influences to surface defect arising from either coatings filling of crack tip or surface roughness. *E*_f and *E*_c are Young's modulus of fibre and coatings, respectively. Notably, the critical tensile stress of fibre with a surface flaw, $\overline{\sigma}_f$, is significantly affected by the coating modulus and thickness. Generally speaking, the thicker the coating layer and larger the stiffness of coatings the higher is the tensile strength of the fibre. On the other hand, the larger the size of defect and higher the stiffness of fibre, for effective repairing, the thicker and stiffer coatings are required.

3.2 Nano reinforcements on fibre surfaces: Electrical properties

Next, we present the results of the electrical resistance measurement of single glass fibre coated with anionic dispersant individualized MWCNTs (Fig. 5). The measured DC resistances *R* of the single MWCNTs-glass fibre are in the range of 104 up to 107 Ω . It in general increases with increasing electrode-electrode distance, *L*. Accordingly, the calculated specific conductivity $\sigma_{glass} = 4L/\pi Rd^2$, for our MWCNTs-glass fibre with diameter of *d*, is typically in the range of 0.1 up to 30 S m⁻¹ and the fibre surface resistance values are in the range of 10³ to 10⁷ Ω /sq. The data presented here could be explained most readily if it is assumed that there is a nanotube layer with a thickness, *t*, on fibre surface having electrical conductivity, σ_{cnt} . The specific conductivity of MWCNTs-glass fibre, σ_{glass} , parallel to the fibre axis is therefore given by:

$$\sigma_{glass} = 4\left(\frac{t}{d} + \frac{t^2}{d^2}\right)\sigma_{cnt} \approx \frac{4t}{d}\sigma_{cnt}$$
(2)

Taking a rough estimate, an average glass fibre diameter $d = 17 \ \mu\text{m}$ and t is in range of a few tens to a few hundreds of nanometres based on fibre surface roughness data, we see the ultra-thin nanotube networks with $\sigma_{cnt} = 10^2$ to $10^3 \ \sigma_{glass} = 10$ to $10^4 \ \text{S} \ \text{m}^{-1}$. It possesses conductivities approaching to the highest values, typically 10^4 to $10^5 \ \text{S} \ \text{m}^{-1}$, of the nanotube only buckypapers achieved with an aggregate of high dense carbon nanotube networks. It suggests that the high conductivity is reached for the carbon nanotube networks with locally isotropic and inhomogeneous distribution on our MWCNTs-glass fibre surface. FE-SEM image (Fig. 5) show that the MWCNTs present in the form of closely packed and highly entangled network structure on the curved fibre surface. The aggregated and individual carbon nanotubes could be clearly seen, which create the conductive pathways.

3.3 Nano reinforcements in composite interphase: structure, adhesion and functionalization

The question of whether the nanoscale semiconductive interphase between glass fibre and epoxy matrix could be experimentally observed is interesting. Our work highlights the importance of no-contact LiftMode electric force microscopy (EFM) as highly sensitive analytical tools in characterisation of interphase. To assess the variation in properties across the interphase, we investigated the cross-section of MWCNT-glass/epoxy composites by both EFM and FE-SEM (Fig. 6). The ultra high resolution FE-SEM image shows clearly many particles in the interphase region with size from approximately ten to several tens of nanometers, which are likely resulted from the exposed ends of nanotubes. To further examine and confirm, we examined the interphase by EFM (Fig. 6b,c), which allows the imaging of relatively weak but long range electrostatic interactions arising from the semiconductive interphase while minimizing the influence of topography since the tip has a distance of 50 nm from sample surface (Fig. 6c). The EFM images were created by the phase shifts, arising from the interactions changing the oscillation phase of the AFM cantilever by applying a voltage between an ultra sharp conductive AFM tip and the interphase. It is clear that the EFM image shows apparent contrast between the fibre, interphase and matrix regions, revealing a difference in the material properties of these three regions. The transition "river-like" layer along the fibre surface is attributable to MWCNTs in the quasi-2D confined interphase region with irregular shape of thickness ranging from 20~500 nm



Fig. 5. Electronic transport property of individual single MWCNTs-glass fibre. a) Schematic diagram for the measurements. The upper optical image of the glass fibre between two Cu electrodes. The low and high-magnification FE-SEM images highlight an inhomogeneous distribution and randomly oriented interpenetrating MWCNT network structure on the glass fibre surface. b) The resistance *R* (white bars) and the specific conductivity σ_{glass} (black bars) versus length *L* of MWCNTs-glass fibre. Error bars, s.d.



Fig. 6. a) FE-SEM and b) EFM images of MWCNT-rich interphase in MWCNT-glass/epoxy composite; c) schematic diagram for electrical mapping cross section of composites with MWCNT-rich interphase by EFM; d) typical nanoindentation force curves on fibre, interphase, and epoxy represent the cantilever deflection signal for one complete extension/retraction indentation cycle of the piezo. The initial slope *k* of the retracting curve represents the cantilever deflection). A softer material would result in less deflection of the cantilever under a given indentation displacement, which provides qualitative information about the elasticity of specimen surface. The slope of indentation on the interphase showing higher value than that of indentation on the epoxy matrix actually demonstrates the higher stiffness of interphase.

and above, which is further confirmed by higher contact stiffness at this region in comparison with that of bulk matrix by nanoindentation (Fig. 6d). The higher stiffness of the interphase determined from the slope of curve in Figure 6d is related to contribution from the intrinsic high stiffness of nanotubes. The combination of high conductivity and high stiffness within interphase is not found for other reported CNT/polymer composites.

The next work focuses on detecting local thermal properties at sub-100 nm resolution. The nano-TA is a newly available local thermal analysis technique which combines the high spatial resolution imaging capabilities of atomic force microscopy with the ability to obtain understanding of the thermal behaviour of materials, such as melting or glass transitions with a spatial resolution of sub-100 nm. In this test, the probe in contact with the polymer is deflected, as its temperature is ramped up, and the cantilever sensor displacement in the Z-axis is measured. As the material under the probe is heated it expands, deflecting the probe upward. The surface layer of the polymer then softens leading to plastic deformation under mechanical pressure of the probe. The preliminary results shown in Fig. 7 suggest an increase of the local glass transition temperature as well as a reducing remarkably downward deflection of the probe tip (much smaller penetration holes) in interphase regin, especially in distance less than 500 nm from the fibre surface. This increasing T_g assigned to the interphase is probably a consequence of a greater enrichment of amines adsorbed by both nanotube and glass fibre surfaces, resulting higher crosslink density in the interphase region.

The fragmentation test has been used for assessing interfacial shear strength, where the tensile load in the specimen is transferred to the fibre by shear stresses in the matrix through the interphase. The fibre keeps breaking until the fragments become too short to build up sufficiently high tensile load to cause further fragmentation with increasing specimen strain. As expected, the control fibre without MWCNTs had the highest critical aspect ratio, which corresponded to the lowest interfacial shear strength. In contrast, the interfacial shear strength was enhanced by the MWCNT coating, particularly the sample with Glymo achieved the maximum interfacial shear strength. The reason of enhancement might arise from different nanotube related toughening mechanisms, including glass fibre/nanotube/matrix interfacial debonding, nanotube pull-out, interfacial crack bridging, etc. The micro-mechanical interlocking contributes mainly to the frictional bond after fibre debonding, an effect similar to the clench of gears may exist between CNTs and cross-linked epoxy molecules. The potential chemical reactions between epoxy and the carboxy-functionalized MWCNTs as well as hydrogen bonding contributed to the improvement of the interfacial strength as well. In presence of silane coupling agent, the reactions of epoxide-carboxy, epoxy-amine, and silanolsilanol gave rise to chemically covalent bonds around glass fibre, MWCNT, surfactant, and epoxy.

Furthermore, the morphology of MWCNT coating on the fibre surface influenced interfacial shear strength. In these cases, the irregular MWCNT distribution along the fibre causes nonuniform interphase structures and properties (strength/stiffness). We then proposed three different interphase structures: (1) homogeneous interphase; (2) mid-homogeneous interphase; (3) inhomogeneous interphase. Fig. 8 shows the birefringence patterns under polarized light of single fibre model composites together with the schemes for these proposed interphases and the stress profiles along the fibre when the fragment number reached saturation. Clearly, the stress birefringence of control fibres and DIP-coated fibres suggests that the interphase suffered from extensive shear stresses and the crack tended to expand along the interphase. Through focusing on the fibre break point, the apparent matrix crack failure mode could be observed in the coated fibre samples, which indicated improved



Fig. 7. Nano-TA thermal analysis on a MWCNTs-glass fibre/epoxy resin composite: Sensor height position response versus temperature for different positions from interphase close to glass fibre towards bulk resin. Associated penetration holes shown in AFM topography becoming bigger with increasing distance from the fibre surface.

interfacial strength due to the presence of the MWCNT coating. The control fibre with homogeneous surface possessed the highest value of the Weibull shape parameter *m*, suggesting uniform interfacial adhesion (Zhang et al., 2010). The interphases for fibres treated by EPD method were classified into the mid-homogeneous, since their Weibull shape parameter value is between control fibre and DIP fibre. Due to the differences in thickness of the MWCNT layers or the heterogeneous adhesion modes from MWCNTs or Glymo, the reinforcement effect was unequal along the whole fibre. Both strong bonding and relatively weak bonding coexist, leading to wider distribution of fragment lengths. It is interesting to note that the coexistence between strong interphase and weak interphase is similar to the biologic bone structure. Besides the apparent reinforcement effect from the strong interphase, the weak interphase serves to inhibit crack propagation or acts as mechanical damping elements [Gupta et al., 2005]. Consequently, the mid-homogeneous interphase with EPD fibre has the strongest interfacial strength which was confirmed by the shortest fragment length.

To provide an unique opportunity for the in-situ load and damage detection, we have exploited the self-diagnosing effects, as pilot approach, of semiconductive MWCNT-glass fibre in composites during tensile test. Fig. 9 shows the electrical resistance and stress as a function of applied strain. We identified basically three stages of resistance variation in i) linear, ii) non-linear, and iii) abrupt changes. At the first stage, the linear behaviour of the



Fig. 8. Three kinds of stress profiles along the fibre axis as a function of position when fracture number reaches its saturation; the birefringence patterns are shown by cross-polarized light for saturation at a magnification of ten. Insert images are the enlarged views of broken points, the interfacial debonding failure mode for control and the matrix crack failure mode for EPD-G and DIP systems were observed.



Fig. 9. Simultaneous change of electrical resistance and stress as a function of strain for single coated fibre/epoxy composite, the dashed *S* is the straight line simulation of $\Delta R/R_0$ at the linear increasing stage. Inserted figures are the photoelastic profiles during tensile process corresponding to the $\Delta R/R_0$ value at the stages of original, linear, non-linear, fibre fracture and composite fracture.
electrical resistance increased proportionally with strain up to approximately 1.5 %, which is possibly linked to the elastic deformation of the interphase. For strains higher than 1.5 % the slope of the resistance-strain curve increased exponentially with strain. This exponential behaviour of resistance change is related to the interphase plastic deformation of CNT networks, associated with stress concentration before fibre breakage, increase of nanotubenanotube interspace and loss of junction points arising from permanent change in network shape during loading. This interphase deformation possibly caused irreversible resistance changes. At the third stage, the interphase failed completely and the resistant jumps "infinite" (The resistance exceeds measurable range). Finally, after interphase fracture, the coated fibre/epoxy composites failed at a strain of about 3.4 %. An important feature occurring in the measurements is that the three stages of the resistance variation are highly consistent and reproducible, thus making such single coated glass fibre as a small and sensitive rapid response mechanical sensor. Overall, our results show that the MWCNT coated fibre/epoxy composites possess a semiconductive interphase and the composite inherent damage can be monitored by measuring changes in electrical resistance in the early stage of damage. The piezoresistive effects of semiconductive MWCNTs-glass fibre and composites, therefore, provide a unique opportunity for an in-situ load and damage detection of the most widely used GFRPs, which, unlike other attempts, does not require additional sensors and dispersion of CNTs in polymer matrix.

We finally turn our attention to how the resistance of the interphase is sensitive to temperature and T_g of polymer (Fig. 9). The resistance decreased monotonically with the increase of temperature, indicating a negative temperature coefficient (NTC) effect which reflects a typically semiconductive characteristic of the used MWCNTs. Most notably, we found a distinct transition on the $\Delta R/R_0$ curve from around 343~347 K, which was almost coincident with the glass transition temperature, $T_g \approx 341 \sim 344$ K shown in the curve measured by DSC. The transition of epoxy network at T_g possibly induces break of some nanotube junction points and elongation of the interspaces between the CNTs, resulting in the variation of the resistance trends. Here, we can infer that the transition temperature detected through the semiconductive interphase is related to the brittle-ductile transition of epoxy in or near interphase when the temperature increases up to T_g . In turn, such transition at T_g could induce variations of thermal residual stresses existing on the interface due to the coefficient of thermal expansion (CTE) mismatch between glass fibre and epoxy. The aforementioned nano-TA results suggest that the entangled nanotube network influences the local cross-linking density of epoxy in interphase resulting in a little different T_g of interphase to that of bulk matrix.

4. Conclusion

A nanometer-scale hybrid coating layer based on styrene-butadiene copolymer with single or multi-walled carbon nanotubes (SWCNTs, MWCNTs) and/or nanoclays, as mechanical enhancement and environmental barrier layer, is applied to traditional glass fibres. The nanostructured and functionalised glass fibres show significantly improved both mechanical properties and environmental corrosion resistance. With low fraction of nanotubes in sizing, the tensile and bending strength of healed glass fibre increases remarkably. Besides, nanocomposite coatings result in enhanced fibre/matrix interfacial adhesion, indicating nanotube related interfacial toughening mechanisms. An increase of the local glass transition temperature in interphase regin, especially in distance less than 500 nm from the fibre surface was found, indicating higher crosslink density. The electrically insulating glass fibre deposited by MWCNTs leading to the formation of semiconductive MWCNT-glass fibres and in turn multifunctional fibre/polymer interphases. Our approach demonstrates for the first time that the techniques of conducting electrical resistance measurements could be applicable to glass fibres for in situ sensing of strain and damage; the techniques were previously limited to conductive and semiconductive materials. The electrical properties of the unidirectional fibre/epoxy composite show linear or nonlinear stress/strain and temperature dependencies, which are capable of detecting piezoresistive effects, early warning of fibre composite damage, as well as the local glass transition temperature. Based on our approach, the glass fibre—the most widely used reinforcement in composites globally—along with the surface electrical conductivity of MWCNTs will stimulate and realize a broad range of multifunctional applications.



Fig. 10. Variability and trends of electrical resistance to temperature for MWCNTs-glass fibre/epoxy composites. The temperature dependence of $\Delta R/R_0$ and heat flow curve (black) obtained by the DSC. Note, the two different methods show similar transitions on the curves in the region of the glass transition temperature of epoxy.

5. References

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Part 4

Gas Sensor

Nanocomposite Films for Gas Sensing

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1. Introduction

Nanocomposite films are thin films formed by mixing two or more dissimilar materials having nano-dimensional phase(s) in order to control and develop new and improved structures and properties. The properties of nanocomposite films depend not only upon the individual components used but also on the morphology and the interfacial characteristics. Nanocomposite films that combine materials with synergetic or complementary behaviours possess unique physical, chemical, optical, mechanical, magnetic and electrical properties unavailable from that of the component materials and have attracted much attention for a wide range of device applications such as gas sensors. Recently, various nanocomposite films consisting of either metal-metal oxide, mixed metal oxides, polymers mixed with metals or metal oxides, or carbon nanotubes mixed with polymers, metals or metal oxides have been synthesized and investigated for their application as active materials for gas sensors. Design of the nanocomposite films for gas sensor applications needs the considerations of many factors, for example, the surface area, interfacial characteristics, electrical conductivity, nanocrystallite size, surface and interfacial energy, stress and strain, etc., all of which depend significantly on the material selection, deposition methods and deposition process parameters. This chapter will summarize recent developments in this new area of research including the fabrication methods currently in use for preparing nanocomposite films, transduction mechanisms for nanocomposite film gas sensors, types of the nanocomposite films suitable for gas sensors application, and the unique gas sensing properties of nanocomposite films.

2. Nanocomposite film fabrication methods

Materials can be deposited in the form of thin film (up to a few micrometer thick) on a substrate by a variety of methods such as physical vapour deposition, chemical vapour deposition, wet-chemical processes such as sol-gel and electrochemical deposition, thermolysis and flame spray pyrolysis etc.. Structural properties and composites of the nanocomposite films are strongly dependent on deposition techniques and deposition parameters. There are many more challenges to deposit composite films consisting of materials of very different nature such as a metal with a polymer or a metal oxide with a metal, than to deposit films of only one type of material. Any deposition process that can be used to prepare nanocomposite films should be able to simultaneously vaporize or coat materials of different nature onto the same substrate to form the composite films. To deposit

composite materials of different natures by precisely controlling their chemical composition, surface morphology, microstructure, and phase remains a challenge. This section will summarize the most common deposition methods used for the fabrication of nanocomposite films for gas sensor applications.

2.1 Physical vapor deposition

Physical vapour deposition (PVD) is referred to a variety of vacuum deposition methods that are used to deposit thin films by the condensation of the vaporized form of materials onto various substrate surfaces. The coating method involves only purely physical processes such as high temperature vacuum evaporation using electron beam or resistance heating, plasma sputter bombardment and pulsed laser deposition. To deposit nanocomposite films by PVD processes, the energy sources, such as electron beam, laser, and plasma, must be able to vaporize component materials under the same processing parameters such as power, energy, temperature and vacuum level, and then condense them at the same time onto a substrate surface to form the composite film.

Sputter deposition is one of the PVD processes that uses a sputtering gas such as argon to sputter composite material sources (a target consisting of pre-mixed compounds or a few targets simultaneously sputtering by ions) which then deposits them onto a substrate to form thin films. Nanocomposite films consisting of mixed metal oxides, a metal and a metal oxide, or a metal and a polymer can be deposited by the sputtering method. Pulsed laser deposition (PLD) is another PVD process that can be used to deposit nanocomposite films. The PLD uses a high power focused pulsed laser beam to ablate targets of materials to be deposited to form a deposited thin film on the substrate inside a vacuum chamber. Since laser beams are much easier to transport and manipulate, and does not interact with gasphase species, the dynamic range of deposition pressures is the largest compared to other vacuum deposition processes. Typical laser wavelengths used in PLD process are less than 250 nm. In such short wavelength, virtually any material can be laser evaporated leading to the possibility for depositing composite films consisting of a variety of materials. Nanocomposite thin film material can be easily deposited by PLD using a target consisting of pre-mixed powder of source materials or ablating multiple targets of different materials simultaneously. The ability of the technique to reproduce the target composition is a unique feature for controlling the composition of nanocomposite films. Fig. 1 shows a typical PLD apparatus used for deposition of Au-WO3 nanocomposite films. The KrF laser beam, operating at 248 nm wavelength, was used to subsequently ablate a rotating WO₃/Au composite target, which was formed by mounting a pie-shaped piece of Au target over a circular WO_3 target as shown in Fig. 1. The vapours from both Au and WO_3 are condensed and mixed on a substrate to form the Au-WO₃ nanocomposite film. To improve the film homogeneities, the substrates were rotated along the vertical axis at a speed of 35 rpm (Yang, 2008). High temperature vacuum evaporation is also a PVD process suitable for depositing nanocomposite films. This technique consists of pumping a vacuum chamber to low pressures and heating the material to produce a flux of vapour and condensing it onto a surface. The material to be vaporized is typically heated by using an electrically resistive heater or electron beam until its vapour pressure is high enough to produce a flux. For depositing nanocomposite films, powders of two or more materials were mixed and compressed into pellets for evaporation. It is also possible to vaporize multiple pellets of different materials using multiple heating sources. The flux of each material can be controlled individually by increasing or decreasing the power of the heating source or exposed area of the materials in the vacuum. Vacuum evaporation is very useful for nanocomposite thin film fabrication due to ease of uniform mixing over a wide range of concentrations.



Fig. 1. A typical PLD apparatus used to deposit nanocomposite films. The laser beam subsequently ablates rotating WO_3 /Au composite targets to produce the Au-WO₃ nanocomposite films

2.2 Sol-gel and other wet chemical synthesis

The sol-gel process is a wet-chemical technique that is widely used to deposit nanocomposite films. In this process, sol (or solution) containing sources for component materials, such as metal alkoxides and metal chlorides precursors for metal oxides, metallic nanoparticles for metals, tetraethoxysilane for silica matrix, catalysers, stabilizers and other additives for porosity generation, was prepared first. The sol then undergoes hydrolysis and polycondensation reactions to evolve gradually towards the formation of a gel-like network containing both a liquid phase and a solid phase. The basic structure or morphology of the solid phase can range anywhere from discrete colloidal particles to continuous chain-like polymer networks. The formation of the nanocomposite film from the sol-gel precursor involves either dip coating or spin coating on a substrate, decomposition and pyrolysis of organic compounds, removal of water and residual organics from the resulting network followed by nucleation and growth of the crystallites. The thermal decomposition behaviour of the gel precursor plays an important role in crystallites size and in film porosity. Sol-gel is an excellent technique for preparing high purity multicomponent films. Various types of nanocomposite films have been prepared by the sol-gel process and used as active materials for gas sensors.

Beside sol-gel process, other wet chemical processes were also used to synthesize nanocomposite films. For example, successive ionic layer deposition (SILD) method was used to prepare SnO₂-Au nanocomposites using HAuCl₄ and SnCl₂ as the precursors (Korotcenkov, 2009). The SILD method consists essentially of repeatedly successive treatments of the substrate surface with solutions of various salts such as acetates, chlorides,

and nitrates of various metals. Electrophoretic deposition process is another wet-chemical process used to incorporate metal nanocrystals into the mesoporous metal oxide films to form metal-oxide nanocomposites films. In the process, the mesoporous metal oxide films are immersed in metallic nanocrystal dispersion. Under applied electrical potential, metallic nanocrystals are infused into the inside of mesoporous oxide film to form the nanocomposite films.

2.3 Chemical vapor deposition and flame spray pyrolysis

Chemical vapour deposition (CVD) is a chemical process that can be used to produce thin nanocomposite films. In a typical CVD process, the substrate is exposed to more than one volatile precursor, which reacts and/or decomposes on the substrate surface to produce the desired composite films. However, only few papers reported using the CVD process to produce nanocomposite films for gas sensor applications. Flame spray pyrolysis is a one step combustion process of solution precursors to produce nanocomposite materials of mixed oxides. Particle size can be produced in the range of 10 nm to 100 nm depending on process parameters. A binder and solvent were then used to mix the nanocomposite particles prepared by pyrolysis to form a paste prior to doctor-blade coating on the substrates to form thin films or thick films for gas sensor applications.

3. Transduction mechanisms for nanocomposite film gas sensors

A gas sensor is an electronic device that consists of a transducer and a sensitive element (an active layer such as a nanocomposite film) that relies, for its operating mechanism, on one of its physical and chemical properties. Basically it operates as follows: a charge transfer occurs between gas molecules and the "sensitive" nanocomposite films, resulting in an electrical and/or optical signal that is related to the gas molecules type and number. Due to its nanoscale morphology and aggregation, the surface-to-volume ratio and quantum confinement, nanocomposite "sensitive" films with high sensitivities, improved selectivity and reduced operating temperatures have been demonstrated. The following section summarizes various types of transducers that utilize different operating mechanisms for the nanocomposite film gas sensors.

3.1 Chemoresistive sensors

Chemoresistive response of nanocomposite films is based on the modification of electrical conductivity of the nanocomposite films due to adsorbed gas species. Chemoresistive effects are perhaps the most attractive measurable responses since very precise readings may be achieved with minimal electronics. To fabrication a chemoresistive gas sensor, nanocomposite films are deposited on to a substrate provided with interdigital electrodes made from either Pt or Au. A thin film heater made from Pt or NiCr is always fabricated on the backside of the substrate as a heater to provide high operating temperature requirement. The resistance of the nanocomposite film is monitored when the film is exposed to difference gases. A typical apparatus for testing chemoresistive gas sensor is shown in Fig. 2. The sensor under test was loaded in a glass chamber and the electrical resistance of the sensor was measured by a multi-meter through two conductive needles when a target gas was injected into the chamber. Chemoresistive response is the most common transduction mechanisms for gas sensors based on nanocomposite films.



Fig. 2. Apparatus for testing chemoresistive gas sensor

3.2 Optical sensors

Optical gas sensors are based on the modification of optical responses of a nanocomposite film induced by interaction with gas molecules. This approach presents a number of advantages over the chemoresistive sensor. Electromagnetic waves are described by a certain number of degrees of freedom such as intensity, wavelength, and polarization: optical sensing thus allows multi-parametric detection, which is not possible in electrical sensing where only a single scalar quantity (electrical conductivity) is involved. Optical sensors do not need electrical contacts, do not suffer from electromagnetic noise and may allow optoelectronic integration and have the potential of multi-gas detection. Different optical responses may be involved in optochemical gas sensing, such as reflectance, absorption, surface plasma resonance or photoluminescence. Examples of optical sensors include white light interferometry of polymer nanocomposite films to measure their swelling sensitivity when exposing to gas vapours (Mauro, 2009), optical absorption of Au-TiO₂ nanocomposite films for the detection of CO and H₂ (Buso, 2008), and surface plasmon resonances of the metal nanoparticles in metal-metal oxide nanocomposites (Yang, 2008 & Fernández, 2005 & Manera, 2008). Recently, nanocomposite films with gas sensing functionality have become a new area of interest for optical gas-sensing applications.

3.3 Surface acoustic wave sensors

The operational principle of an acoustic wave gas sensor is a travelling wave combined with a confinement structure to produce a standing wave whose frequency is determined jointly by the velocity of the travelling wave and the dimensions of the confinement structure. Surface acoustic wave gas sensors obtain their gas sensitivity from a chemically active nanocomposite film coated on top of the acoustic device, which interacts with the surrounding gases. The acoustic wave travelling in the coated device particularly penetrates into the adjacent composite film, translates and deforms the film, thereby probing its mechanical properties, its thickness and the acoustic properties at the upper film surface. The chemical interaction on the surface of a nanocomposite film leads to a change in acoustic wave propagation, which in turn yields a change of the electrical response of the sensor. The quartz crystal resonator is the most common device used as an acoustic-wave-based sensor. The simple geometry of the device and the predominant thickness-shear mode of the propagating wave are propitious conditions for a comprehensive derivation of the acoustic-electrical behaviour of quartz crystal devices. Examples of surface acoustic wave gas sensors using nanocomposite films include TiO₂-porphyrin nanocomposite thin film coated on a quartz crystal was used to detect volatile organic compounds such as ethanol, acetone, 2-propanol, cyclohexane, toluene and o-xylene (Arshad, 2008) and a polyaniline-indium oxide nanocomposite thin films gas sensor was fabricated on AT-Cut quartz crystal microbalance (QCM) of Ag electrodes for analyze CH₄ and CO gases (Yan, 2009).

4. Types of nanocomposite films

Nanocomposite films consists of nanocrystalline or amorphous phase of a least two different materials. Depending on the nature of the component materials, micro/nanostructure and surface/interfacial characteristics, various unique gas sensing properties can be realized by using nanocomposite films as the active layer. Improvement in gas sensitivity, selectivity, stability, as well as reduction in the response time and operating temperature has been demonstrated by various types of nanocomposite films. In the following section, the fabrication and unique gas sensing properties of various types of nanocomposite films such as metal-metal oxide, mixed metal oxides, polymers mixed with metals or metal oxides, or carbon nanotubes mixed with polymers, metals or metal oxides will be described.

4.1 Metal-metal oxide nanocomposite films

Nanocomposite films that consist of metal nanoparticles dispersed in a matrix of metal oxides have recently attracted much interest as materials for gas sensors. Metal-metal oxide nanocomposites have physical properties that differ from those of the nanostructured single phase metal oxides. The metal nanoparticles play both passive and active roles in the sensing process. The presence of metal nanoparticles increases the active surface area and improves gas diffusion inside the film. Metal nanoparticle also reduces the electrical resistance and increases the optical absorption of metal oxide. Metal nanoparticles such as platinum (Pt), palladium (Pd), gold (Au), palladium (Pd) and silver (Ag) also show catalytic properties that can modify the analyte-metal oxide chemical interactions and enhance the sensing process. The interfacial region between metal nanoparticle and metal oxide also has very different electron band structure than inside the bulk semiconducting metal oxide, which also contribute to the unique gas sensing properties of this type of nanocomposite.

Fabrication

The amount and distribution of the metallic nanoparticles in a metal oxide matrix is an important parameter to be controlled in order to obtain highest gas sensing sensitivity. Diverse methodologies including PVD, impregnation, sol-gel, and electroless plating have been used to introduce metal nanoparticles into the metal oxide matrix. For example, reactive magnetron sputtering was used to deposit Pd-doped SnO₂ nanocomposite films with tetragonal SnO₂ structure and columnar nanograins at the substrate temperature of 300 °C and discharge gas pressure of 1.5, 12, and 24 Pa. The discharge current was fixed at 80

mA, and the discharge voltage showed a value between 280 and 260 V, depending on the discharge gas pressure. It was found that a porous film could be formed at a high discharge gas pressure and a low substrate temperature (Shen, 2009). Metal-metal oxide nanocomposite films can also be deposited by the PLD. For example, gold-zinc oxide nanocomposite films have been synthesized by subsequent laser ablation of zinc and gold targets using either an UV KrF excimer or a frequency tripled Nd:YAG laser. The optical properties of the gold-zinc oxide nanocomposite films can be tailored by proper choice of the relative number of laser pulses used for the ablation of the gold or zinc targets (Gyorgy, 2008). Surface plasma resonance (SPR) gas sensors using very thin Au-WO_{3-x} nanocomposite thin films were also fabricated by PLD and the content of Au in the composite films was also varied by altering the relative laser ablation time on Au and WO₃ targets, respectively (Yang, 2008).

Dot- and rod-shaped Au-TiO₂ nanocomposite films were prepared by a sol-gel method for SPR sensing of alcohol vapours. For the synthesis of Au-TiO₂ nanocomposite films, firstly, a sol using titanium isopropoxide, isopropanol and acetic acid with a molar ratio of 1:6:1.3 was prepared. Then, a colloidal solution containing Au spherical nanoparticles was prepared and mixed with the sol. Colloidal gold was synthesized by reducing HAuCl₄ with tris-sodium citrate in water and then dispersed in ethanol by using poly(nvinylpyrrolidone) as a stabilizer. The mixed sol was spin coated onto fused silica slides following by drying and heat treatment to form the thin films (Manera, 2008). Other metal-metal oxide nanocomposite films prepared by sol-gel processes include the SnO₂-Ag nanocomposite (Gong, 2006); Au-TiO₂-NiO nanocomposites (Gaspera, 2010) and Au-TiO₂ nanocomposite films for sensing vapour organic compounds by Surface Plasmon Resonance and optical absorption (Fernandez, 2005). Beside sol-gel process, other wet chemical processes were also used to synthesize metal-metal oxide nanocomposite films. SnO2-Au nanocomposites were deposited by the SILD method on a substrate coated with un-doped SnO₂ films of thickness \sim 50-55 nm using HAuCl₄ and SnCl₂ as the precursors. The thickness of the SnO₂-Au nanolayer on the surface of the SnO₂ films was controlled through the number of deposition cycles (Korotcenkov, 2009). A significant limitation in SILD deposition relates to the repeated treatment of the growing film, which is necessary for the synthesis of the multilayer, but it can cause re-dissolution of the film in the solution during repeated treatment. Electrophoretic deposition process can also be used to deposit metal-metal oxide nanocomposite films. For example, the mesoporous TiO₂ on ITO/glass was immersed in Au nanocrystal dispersion in chloroform. A potential of 25 or 50 V was applied to infuse the Au nanocrystals inside the mesoporous TiO₂ film to form the Au-TiO₂ nanocomposite films. The ligands such as dodecanethiol on the Au nanocrystals prevented aggregation. The films were highly conductive, and are suitable for sensor applications (Patel, 2007 & Mehul, 2008).

Unique properties

Metal-metal oxide nanocomposite films combine the catalytic property of metal and gas reactivity of semiconducting metal oxide, thereby possess unique gas sensing properties unavailable from either the metal or metal oxide alone. Metallic nanoparticles activate or dissociate the detected gas on their surface. These activated products are easier to react with the adsorbed oxygen species on the metal oxide surface, resulting in a change of resistance. In addition, direct exchange of electrons between the semiconductor metal oxide and metallic nanoparticles causes a change in the width of the depletion layer of the semiconductor oxide, leading to a change in sensing properties. The embeded metal nanoparticles can reduce the sensing temperatures, improve the selectivity, and increase the surface area of the metal oxide.

Sun et al. (Sun, 2009) investigated the Pd-doped SnO_2 nanocomposite films for H_2 gas sensing. They found that the composite films show reversible response to H_2 gas and their sensitivity is better than undoped SnO_2 films. Fig. 3a shows the sensitivity of undoped and Pd-doped SnO_x thin films measured at 100, 125 and 150 °C when exposed to 250 ppm H_2 . The Pd-doped SnO_x has a sensitivity about one or two orders of magnitude higher than the undoped SnO_x at each temperature investigated. Fig. 3b shows the response transients of two films at 150 °C. For undoped and Pd-doped SnO_x thin films, the response time was 14 and 10 min, respectively. Clearly Pd-doped SnO_x reduces the response time.



Fig. 3. (a) H_2 gas sensitivity of undoped and Pd-doped SnO_x thin films measured at different temperatures. (b) Response transients of both films obtained at 150 °C. The concentration of H_2 is 250 ppm diluted in N_2 (Sun, 2009).

The influence of Pd doping on the microstructure of SnO_x thin films was investigated by SEM and TEM. Fig. 4a and b shows the SEM secondary electron images of undoped and Pddoped films, respectively, while the corresponding TEM images are shown in Fig. 4c and d. It is clear that the undoped film has larger pores and grain size than the Pd-doped film. The histograms of the grain size distributions measured by TEM are plotted in the insets of Fig. 4c and d. The grain size distributions of both films are fitted with a log-normal distribution. The average grain size of the undoped and Pd-doped SnO_x films is 15 and 9 nm, respectively. Knudsen gas diffusion and depletion layer models were employed by Sun et al. to evaluate the microstructure influence on the gas sensitivity. Their results suggest that the microstructure of the Pd-doped film is critical for improving the gas sensitivity, but cannot account for the total sensitivity enhancement. They believed that other mechanisms could also play important role and the electronic and chemical activities of Pd could be the primary factors for the sensing enhancement (Sun, 2009).

Au-TiO₂ nanocomposite films were used by Buso et al. (Buso, 2008) as both optical and chemoresistive sensors for the detection of CO and H₂. Tests performed at 360 °C show COand H₂-induced reversible variations in the optical absorption of thin Au-TiO₂ nanocomposite films. The absorbance changes are strongly dependent on both the testing wavelength and the film microstructure. The reactant gases CO and H₂ were suggested to initially adsorb into the titania matrix. Once oxidized the liberated electrons then flow to



Fig. 4. (a) and (b) SEM secondary-electron images and (c and d) TEM bright-field images of undoped and Pd-doped SnO_x films annealed at 700 °C for 1 h. Grain size statistics from TEM images are shown in the insets of (c) and (d). The distribution was fitted using log-normal probability density function (Sun, 2009).

and are trapped on the gold nanocrystals. Gas adsorption in the matrix sites near the Au nanoparticles could lead to local changes in refractive index of TiO₂, which, in principle, are capable of affecting the absorption spectral changes. Mehta et al. (Mehta, 2005) investigated In₂O₃-Ag nanocomposite films having well-defned individual nanoparticle size and composition for ethanol gas sensing application. For a pure In₂O₃ nanoparticle film with particle size of 11 nm, they observed the sensitivity of 325 and the response time of 8 s at 400°C for 1000 ppm ethanol, while for In₂O₃-Ag nanocomposite film, the sensitivity increases to 436 and the response time is reduced to 6 s. They believed that Ag additives form a p-type Ag_2O_2 , which interact with n-type In_2O_3 to produce an electron-deficient spacecharge layer. In the presence of ethanol, interfacial Ag₂O was reduced to Ag, creating an accumulation layer in In₂O₃ resulting in increased sensitivity (Mehta, 2005). Gong et al. (Gong, 2005) discovered that SnO₂-Ag nanocomposite films have very high sensitive to hydrogen sulfide: as low as 1 ppm concentrations of H₂S at low working temperature of 70°C can be detected by the composite films. The SnO₂-Ag films are also less sensitive to common interference gases such as Cl₂, HCl, SO₂, C₆H₁₄, CH₄, CO, C₃H₈. Korotcenkov et al. deposited a SnO₂-Au nanocomposites film over a pure SnO₂ surface and studied its response to reducing gases such as CO and H_2 (Korotcenkov, 2009). They found that by increasing the thickness of the SnO₂-Au nanocomposite layer, the sensor response and the recovery times were decreased. The ZnO films with embeded noble-metal nanoparticles (Pt, Au and Ag nanoparticles) also exhibit enhanced sensitivity and fast initial recovery behavior compared to those without metal nanoparticles (Mishra, 2005).

Due to the localized surface plasmon resonance (SPR) of the metal nanoparticles, metalmetal oxide nanocomposite films can also be explored as plasmonic-based optical gas sensor using their unique optical properties. SPR responses of Au-WO_{3-x} and Ag-WO_{3-x} nanocomposite films with either stoichiometric (x = 0) and non-stoichiometric (x > 0) structures were simulated using effective medium theory and Macleod's general characteristic matrices method for various metal percentages and film thicknesses in the Kretschmann configuration at the wavelength of 632.8 nm. The simulation results predicted that the Au-WO_{3-x} and Ag-WO_{3-x} nanocomposite thin films with 40-80% metal fractions and film thickness of 30-50 nm are applicable for optical gas sensing (Deng, 2008). We also observed that SPR response of Au-WO3-x nanocomposite films changed when exposed to low ppm of NO gas which indicated that gas sensing using the SPR responses of metalmetal oxide nanocomposite films is feasible (Yang, 2008). Thin films composed of Au nanoparticles dispersed inside a TiO2-NiO mixed oxide matrix were also inverstigated by Gaspera et al. (Gaspera, 2010) as hydrogen sulfide optical sensors using the Au-localized SPR. The detection sensitivity is shown to be down to a few ppm of H₂S, and almost no interference in response is observed during simultaneous exposure to CO or H₂. The high sensitivity and selectivity of the Au-TiO2-NiO nanocomposite film for H2S detection is believed to be due to direct catalytic oxidation of H₂S over the Au-TiO₂-NiO nanocomposite film (Gaspera, 2010). Manera et al. (Manera, 2008) discovered that dot- and rod-shaped gold nanoparticles embeded TiO2 thin films possess optical absorption sensing responses towards different kinds of alcohol vapours in the spectral range corresponding to the SPR peak of the gold nanoparticles. Total attenuation SPR measurements in controlled atmosphere by them revealed that the sensing property is due to variation of the thickness and the real part of the active sensing layer refractive index. Au-TiO₂ film is another metalmetal oxide nanocomposite film that was investigated for optical gas sensing of different vapour organic compounds (Fernández, 2005). All the above results clearly indicate that metal-metal oxide nanocomposite films offer a real opportunity for optical gas sensing with rapid and sensitive response to many common gases.

4.2 Mixed metal oxides

Transition metal oxides have promising gas sensing performance due to their catalytic properties. Some transition metal oxides are stable, have low electric resistance and good gas sensing properties at low operating temperature, while others have high electric resistivity and require high operating temperatures. Some of the oxides are more sensitive to oxidizing gases while others are more to reducing gases. It is therefore a natural approach to combine metal oxides of different properties with an appropriate proportion so that gas sensor performance can be modified as desired.

Fabrication

Although PVD, sol-gel and pyrolysis can be used to deposit mixed metal oxide nanocomposite films, sol-gel method is the most cost-efficient method as it represents a simple processing alternative to the vacuum deposition techniques. Various mixed metal oxide nanocomposite films have been prepared by the sol-gel process. For example, cobalt oxide-SiO₂ nanocomposite films were deposited on glass substrate by Musat et al. (^aMusat, 2008) using $[Co(CH_3COO)_2].4H_2O$, tetraethoxysilane and $CH_3(CH_2)_{15}N(CH_3)_3Br$ surfactant as starting materials. After each layer was deposited on a substrate by dipping, the gel film was dried at 70 °C and then pre-heated in air at 400 °C. The procedure was repeated 2 or 3

times. The stabilized films were then post-heat treated in air at 500 °C for cobalt oxide crystallization. The effect of withdrawal speed, number of layers and thermal treatment on the crystalline structure, morphology, Co-doping states, optical, electrical and gas sensing properties of the thin films were investigated. When using sol-gel process for the deposition of ZnO-SiO₂ nanocomposite films, zinc acetate (Zn(CH₃COO)₂ 2H₂O) was used as the ZnO nanoparticles source, tetraethoxysilane (TEOS) as a silica matrix source and cetyl trimethylammonium bromide (CTAB) as a surfactant for porosity generation. The chemical nature of ZnO source (zinc acetate solid salt, zinc acetate alcoholic solution or ZnO nanopowder) used for the sol preparation was found to significantly affect the thermal decomposition of complex precursor and the microstructure and properties of the nanocomposite thin films (bMusat, 2008). Thin SiO₂-NiO and SiO₂-Co₃O₄ nanocomposite films consisting of either NiO or Co_3O_4 nanocrystals in a porous SiO₂ matrix were also prepared by the sol-gel method, in which one solution containing the silica (mixture of tetraethoxysilane, methyltriethoxysilane, H₂O, HCl and EtOH) was mixed with another solution containing the metal oxide precursor (dissolving CoCl₂ 6H₂O or NiCl₂ 6H₂O in N-[3-(trimethoxysilyl)propyl]-EtOH). 3-aminopropyl triethoxysilane or Either ethylendiamine molecules was added to the solution to coordinate the Co²⁺ or Ni²⁺ cations (Cantalini, 2005). Other mixed metal oxides nanocomposite films prepared by the sol-gel process include SiO₂-NiO films ((100-X)SiO₂-XNiO with X = 10, 20, 40) (^aMartucci, 2003); MoO₃-TiO₂ films (Li, 2001); Fe₂O₃-SnO₂ films for detecting NO₂ and C₂H₅OH gas (Kotsikau, 2004); NiO-SiO₂ films for detection of H₂, CO and humidity (Martucci, 2004 & ^bMartucci, 2003); In_2O_3 -SnO₂ film for detecting H₂ at ppm-level at room temperature (Satyajit, 2005); and Li and Ti co-doped NiO nanocomposites (Li0.1Ti0.018Ni0.882) for detecting toluene, ethanol and chloroform (Qureshi, 2009).

PVD process has also been used to deposit mixed metal oxide nanocomposite films. Wisitsoraat et al. (Wisitsoraat, 2007) used oxygen ion-assisted electron beam evaporation to prepare various TiO₂ based mixed oxide nanocomposite films such as TiO₂-WO₃, TiO₂-MoO₃, TiO₂-NiO_x, and TiO₂-ZnO. They first mixed TiO₂ powder with WO₃, MoO₃, NiO_x, or ZnO powders, and then pressed the mixed powder to form pellets. Electron beam evaporation of the pellets occurs in vacuum chamber to form mixed oxide films. After annealing the films in air at 500 °C, various TiO₂ composite films having nanocrystalline structure with fine grain size ranging from 10-50 nm were prepared. Flame spray pyrolysis was also used to prepare WO₃-doped ZnO nanoparticles (Siriwong, 2009).

Unique properties

Mixing metal oxides of complementary behaviours forms a new class of nanocomposite materials. This type of nanocomposite films show a significant improvement in gas sensing properties. For example, by embedding transition metal oxide nanoparticles such as NiO and Co₃O₄ in a porous silica glass matrix, the nanoporosity of such composite matrix provides a path for the gas molecules to reach the functional ultrafine NiO and Co₃O₄ particles. The sensor response of the NiO-SiO₂ and Co₃O₄-SiO₂ nanocomposite films to H₂ (20-850 ppm) and CO (10-500 ppm) in dry air and at different operating temperatures (50-300°C) has been investigated by Cantalini et.al using both conductometric and optical transmittance transduction methods (Cantalini, 2005). Both the NiO and Co₃O₄ doped films exhibit a conductometric p-type response, with a resistance increase upon exposure to the reducing gas. The nanocomposite films also showed a reversible change in the optical transmittance in the vis-NIR range when exposed to CO (10-10,000 ppm) in dry air. SiO₂-

NiO films have shown the highest response to H₂ at 300°C operating temperature and good selectivity to H₂ when CO is the interfering gas. Selectivity tests shown in Fig. 5 comprise a first exposure (first section) to 200 ppm H₂ target gas in dry air, followed by a second exposure (second section) where the films are subjected to 200 ppm H₂ and to 200 ppm CO interfering gas. In the third section, films are exposed to the interfering gas alone (200 ppm CO). For the SiO₂-Co₃O₄ nanocomposite film, CO slightly increases the film resistance in addition to resistance increase due to H₂ saturation as depicted in the second section of Fig. 5. This effect is totally absent for the SiO₂-NiO film. The lack of CO interfering effects may be explained in terms of a stronger affinity of the H₂ molecules to adsorb on the metal oxide surface (Cantalini, 2005).



Fig. 5. Cross sensitivity test at 300 °C operating temperature of the SiO₂–NiO and the SiO₂– Co_3O_4 films to: (first section) 200 ppm H₂ in dry air; (second section) 200 ppm H₂ in dry air and 200 ppm CO; (third section) 200 ppm CO in dry air (Cantalini, 2005).

Martucci et al. (Martucci, 2004 & Martucci, 2003) has also studied the gas response of SiO₂-NiO and SiO₂-SnO₂ nanocomposite films for H₂, CO and humidity at different operating temperatures ranging from 25 to 350°C and gas concentrations between 10 and 1000 ppm. SiO₂-NiO and SiO₂-SnO₂ nanocomposite films showed a p-type and n-type response, respectively, with greater sensitivity to H₂ gas than CO in the whole range of operating temperatures. The NiO- SiO₂ nanocomposite films also showed a reversible change in the optical transmittance in the VIS-NIR range when exposed to carbon monoxide gas.

Various TiO₂ based mixed oxide nanocomposite films, including TiO₂-WO₃, TiO₂-MoO₃, TiO₂-NiO_x, and TiO₂-ZnO, have been characterized for gas-sensing applications by Wisitsoraat et al. (^bWisitsoraat, 2007). NiO_x addition to TiO₂ with sufficiently high concentration has produced a p-type semiconducting thin film while WO₃, MoO₃, and ZnO inclusions result in typical n-type metal oxide semiconductors. The gas-sensing sensitivity, selectivity, and minimum detectable concentration toward different gases including acetone, CO, and NO₂ can be effectively controlled by different dopants and doping concentrations. The p-type NiO_x doped TiO₂ showed high sensitivity towards ethanol and acetone with

distinct behaviours compared to other n-type TiO₂ thin films. Siriwong et al. (Siriwong, 2009) investigated WO₃-doped ZnO composite containing 0.25, 0.50, and 0.75 mol% of WO₃ for NO₂, CO and H₂ gas sensing at different gas concentrations and operating temperatures ranging from 300-400°C in dry air. Their results showed that WO₃ doping significantly enhanced NO₂ gas sensing performance of ZnO nanoparticles. In addition, 0.5 mol% is found to be an optimal WO₃ concentration which gives the highest sensitivity towards NO₂. Other mixed oxides showing improved gas sensing properties include Cr₂O₃-WO₃ films for NO₂ in NO_x mixtures (Cantalini, 2004), Fe₂O₃-ZnO films for NH₃ (Tang, 2006) and CuO-Cu_xFe_{3-x}O₄ (with 0 < x < 1) for CO₂ (Chapelle, 2010).

4.3 Polymer-metal or metal oxide

Gas sensors using metal oxide films always lack in selectivity and require high operating temperatures (300-500°C). High operating temperatures may leads to sensor instability and response variation. Sensing materials with low operating temperatures can inhibit structural changes, reduces the power consumption and enables safer detection of combustible gases. Conducting polymers such as polypyrrole (PPy), polyaniline (PANI), polythiophene (PTh) and their derivatives typically can operate at low temperature in comparison to most of the metal oxide sensors. Conducting polymers can behave like semiconductors due to their heterocyclic compounds. As a result, reversible changes in the sensing polymer layer's conductivity can be detected upon adsorption of polar gas molecules on the surfaces at low temperature. This effect is believed to be caused by the charge transfer between gas molecules and the polymer or the polymer film's swelling. Conducting polymers are also easy to be synthesized through chemical or electrochemical processes, and their molecular chain structure can be modified conveniently by copolymerization or structural derivations. In addition, conducting polymers have good mechanical properties, which allow a facile fabrication of sensors. Conducting polymer matrices embedded with nano-scale metal or metal oxide particles forms a new class of nanocomposite materials that has shown better gas sensing features. The reasons for such an improvement can be attributed either to catalytic behaviours of metal particles or to the formation of metal oxide-polymer junction. For example, the n-type SnO_2 forms a hetero pn-junction to p-type conducting polymer with a depletion region. The gas adsorption causes a change in depletion region and thus modulates the conductivity of the junction. Other non-conductive polymers such as fluorocarbon films swell when exposed to the vapours of organic solvents having a net dipole moment or electron-rich moieties therefore can also be used as active materials for the gas sensing. Addition of metal or carbon to those polymers was found to improve their swell sensitivity.

Fabrication

Metal-polymer nanocomposites can easily be prepared by PVD processes such as sputter deposition and vacuum thermal evaporation, as well as wet chemical deposition. For example, Tiwari et al. (Tiwari, 2009, & 2010) used vacuum thermal evaporation of poly(o-phenylenediamine) (PoPD)/WO₃.nH₂O mixed powder pellet to fabricate nanocomposite films of PoPD-WO₃.nH₂O on an indium tin oxide (ITO) coated glass surface for NO₂ gas sensor applications. Using the same method; they also prepared aniline-formaldehyde condensate (AFC)-WO₃.nH₂O nanocomposite films. The mixed powder pellets were formed via hydraulically pressing of nanocomposite powders which was prepared by in situ condensation reaction of PoPD or AFC in the presence of sodium tungstate. The composite

thin films exhibited a crystalline surface morphology containing nanocrystalls of $WO_3.nH_2O$ with a diameter ranging from 5 to 20 nm. Cioffi et al. prepared gold-fluorocarbon (Au-CF_x) and palladium-fluoropolymer (Pd-CF_x) nanocomposites films on silicon substrates by co-sputtering a Teflon and a gold targets or a Teflon and a palladium targets, respectively, with Ar⁺ ion beams (Cioffi, 2002 & 2004).

Wet-chemical deposition route can also be used to prepare polymer-metal oxide nanocomposite films, for example, tin oxide-intercalated polyaniline nanocomposite have been deposited at room temperature by Deshpande et al. (Deshpande, 2009) through the following procedure: SnCl₄ 5H₂O was first hydrolyzed at pH \leq 4 using dilute HCl. Hvdrogen peroxide was added to the solution to oxidize tin ions to form tin oxide suspension. The suspension solution was mixed with aniline and (NH₄)₂S₂O₈. Pre-cleaned glass substrates were inserted vertically into the solution for the growth of the nanocomposite film on the substrate. Tin oxide exists as nanoparticles form in the polyaniline (PANI) matrix in the composite films. Intercalation reactions is another wetchemical process used to prepare polymer-metal oxide nanocomposite, for example, polypyrrole (PPy)-MoO₃ nanocomposite thin films have been prepared by the intercalation reactions of highly oriented MoO₃ thin films with the following procedure: hydrated sodium ions were inserted into the CVD grown MoO₃ thin films on LaAlO₃ (100) single crystal substrates to give $[Na(H_2O)_2]_VMoO_3$ films. The obtained $[Na(H_2O)_2]_VMoO_3$ thin films then reacted with an excess amount of pyrrole and oxidizing agent (FeCl₃) to form the (PPy)xMoO3 thin films. Intercalation of hydrated sodium ions successfully proceeded without loosing the crystallographic orientation. The (PPy)_xMoO₃ thin films can detect formaldehyde gas by increasing their electrical resistance, whereas they showed no response to toluene (Hosono, 2004). Tai et al. (Tai, 2007 & 2008) reported using simultaneous polymerization of aniline monomer and oxidation of PANI molecules in an active solution contained colloidal TiO₂, aniline monomer, HCl and oxidizing agent ammonium persulfate ((NH₄)₂S₂O₈) to fabricate the polyaniline-titanium dioxide (PANI-TiO₂) nanocomposite films for NH₃ gas-sensing application.

Unique properties

Polymer-metal or metal oxide nanocomposite is a new class of material that combines the advantages of both organic polymer material and inorganic metal or semiconductor oxide and shows improved optical, electrical and mechanical properties for gas sensor applications. Cioffi et al. (Cioffi, 2004) investigated - CF_x polymer films embedded with Pd or Au nanoparticles (Pd-CFx and Au-CFx nanocomposites films) for detecting vapours of organic solvents. They found that Pd-CFx and Au-CFx nanocomposites films swell more significantly than pure $-CF_x$ film when exposed to the vapours of organic solvents having a net dipole moment or electron-rich moieties such as acetone, chloroform, 2-propanol. Ellipsometric evaluation of the thickness changes of $-CF_x$ and metal-CF_x films when they exposed to an increasing concentration of acetone vapours was shown in Fig. 6(a). All the films show almost linear dependence of the thickness change upon the analyte concentration but -CFx swelling sensitivity is much less pronounced than that of the metal- CF_x composites. Acetone-induced swelling of both Au-CF_x and Pd-CF_x materials increases as the metal loading increases and the swelling response of $Pd-CF_x$ films is higher than that of Au-CF_x of the same metal loading. TEM surface morphology of the Pd-CFx film with a metal loading of 0.15 and 10 nm thick is shown in Fig. 6(b). TEM graphs revealed a regular, non-porous Pd-CFx film structure with homogeneous distribution of palladium



Fig. 6. (a) Acetone-induced thickness variations (Δ t) of Pd–CF_x, Au–CF_x and CF_x layers (metal volume fractions are in brackets) upon exposure to increasing partial pressures of the organic solvent measured by ellipsometry; (b) TEM micrographs of Pd–CF_x films with metal loading of 0.15 (Cioffi, 2004).

nanoparticles. The mean diameter of the palladium nanoparticles is 2.9 ± 0.6 nm. The morphological similarities exist between Pd-CF_x and Au-CF_x films of same metal volume fraction. Differences in the materials sensing performances are ascribed to different chemical reactivity and selectivity of Pd and Au. Swelling behaviour of poly(2-hydroxyethyl methacrylate) (PHEMA)-carbon black nanocomposites was also investigated by Mauro et al (Mauro, 2009) for volatile organic compounds (VOCs) detection using white light interferometry. They demonstrated that swelling in the range of only a few nanometers can be measured and the PHEMA-C nanocomposite undergoes a more pronounced swelling process than PHEMA itself.

Polyaniline (PANI) is a conducting polymer with high electrical conductivity. Due to its ease of synthesis, environmental stability, and response to acid/base doping, it was thoroughly studied for its application as an active material for gas sensors. Mixing semiconductive metal oxide with PANI to form nanocomposites was found to be an effective way to improve the gas sensing properties of PANI. Tai et al. (Tai, 2007) studied a polyanilinetitanium dioxide (PANI-TiO₂) nanocomposite films for the NH₃ gas sensor. They found that the nanocomposite exhibited higher sensitivity, faster response and recovery rates to NH₃ than those of pure PANI thin film sensors fabricated under identical conditions. They found that the TiO₂ components influenced the morphology of the nanocomposite film, which led to the variation of the sensor response-recovery behaviours. Deshpande et al (Deshpande, 2009) discovered that good sensitivity; reproducibility and faster response to NH_3 at room temperature can be achieved by using SnO₂-PANI nanocomposites films while under the same conditions pure SnO_2 films remain inert. They found that resistance of the nanocomposite (SnO₂-PANI) films decreases while pure PANI film resistance increases when exposed to NH₃ indicating SnO₂ doping totally changed the electrical property of PANI. PANi- In_2O_3 was another PANI-oxide nanocomposite films that was thoroughly investigated. The nanocomposite film based gas sensor was fabricated on AT-Cut quartz crystal microbalance (QCM) and its sensitive properties to CH_4 and CO were characterized. They found that PANi-In₂O₃ thin film has good linear sensitive property to CH_4 and CO, and it is more sensitive to CH_4 than CO (Yan, 2009). Misra et al. (Misra, 2004) studied the Fe-Al doped nanocomposite copolymer of aniline and formaldehyde and found that the nanocomposite exhibits high stability, sensitivity, selectivity and a fast response towards the HCl vapours in the air at room temperature. Optimization of doping (Fe-Al) level in nanocomposite copolymer during synthesis can improve the sensing properties.

Other polymer nanocomposite films that were investigated for gas sensor applications include TiO₂-porphyrin film coated on a quartz crystal to detect volatile organic compounds such as ethanol, acetone, 2-propanol, cyclohexane, toluene and o-xylene (Arshad, 2008); poly(vinyl butyral)-carbon black films prepared for methanol, propanol and hexanol vapour (Arshak, 2006); sodium polystyrenesulfonate (NaPSS)-ZnO for humidity sensors (Yang, 2002); polypyrrole (PPy)-SnO₂, PEDT-SnO₂, PHTh-SnO₂ and copolymer (HTh-EDT)-SnO₂ films for NO₂ gas sensing applications (Ram, 2005); poly(3-hexylthiophene)-ZnO films for NO₂, NH₃, CO and ethanol detection (Baratto, 2006); PoPD-WO₃.nH₂O (Tiwari, 2009) and AFC-WO₃.nH₂O (Tiwari, 2010) films for NO₂ gas sensing.

4.4 Carbon nanotube based nanocomposite films

Carbon nanotubes (CNTs) are very useful materials for gas-sensing applications because of their high surface to volume ratio. The large surface area provided by the hollow cores and outside walls in nanotubes gives them very large capacity for gas absorption. Interaction of CNTs with certain gases can change the electrical properties of semiconducting CNTs even at room temperature. However, CNTs based sensor has a number of limitations including long recovery time, and weakness to humidity. In addition, the range of gas molecules that can be detected by CNTs sensors is limited to the molecules that have large binding energies and charge transfers with the CNTs. To improve the gas sensing properties of CNTs, catalytic metal nanoparticles, semiconductive metal oxides or conductive polymers were mixed with CNTS to form nanocomposites. The composite combines the advantages of CNTs and other gas-sensing materials and provide a new class of active materials with unique gas sensing property.

Fabrication

CNTs nanocomposite films can be prepared by combining CVD and PVD processes. For example, Pt-, Ru- and Ag-nanoclusters embedded CNTs nanocomposites were prepared by RF magnetron sputtering and RF-discharge plasma enhanced chemical vapour deposition (PECVD) processes in the following steps: First, iron catalyst film of 2.5 nm thick was deposited by RF magnetron sputtering on alumina substrates using Ar flux of 43 sccm, process pressure of 1.2×10^{-2} Torr and RF power of 150 W. The PECVD iron film was used for the subsequent CNTs growth at a substrate temperature of 600°C with 20/80 sccm C_2H_2/H_2 flow and total pressure of 1.5 Torr. The carbon nanotubes obtained were "forestlike" with ropes vertically-aligned to the substrate surface. CNTs surface has been subsequently modified by depositing 5 nm thick Pt-, Ru- and Ag nanoclusters. The Field emission SEM images of the metal-coated CNTs are shown in Fig. 7(a), (b), and (c), respectively. The metal-catalysts deposited onto the surface of the forest-like CNTs network existed as dispersed islands with non-uniform distribution. To drive metal nanoparticles diffuse into the inside of the CNT-forest, thermal treatment was used. The diameters of metal cluster are ranging from 3 nm for platinum and ruthenium (Fig. 7(a) (c)), to 50 nm for Ag (Fig.7 (b)), which depend on the reactivity between metal and graphite surface (Penza,



Fig. 7. FE–SEM images of the CNT films surface-functionalized with (a) platinum (Pt), (b) silver (Ag) and (c) ruthenium (Ru) nanoclusters (Penza, 2009).

2009). Wisitsoraat et al. (Wisitsoraat, 2006) used electron beam evaporation of cylindrical pellets consisting of pressed multi-wall CNTs (MWCNTs) mixed with SnO_2 powder to form CNTs-SnO₂ nanocomposite films. The CNTs were synthesized by chemical vapour deposition using acetylene and argon gases with iron catalyst at 600 °C. The substrates for thin film coating were standard BK7 glass slides.

Sol-gel process can also be used to prepare CNTs nanocomposites. For example, antimony-CNTs-tin oxide nanocomposite films were prepared with the following procedure: tin(IV) chloride pentahydrate (SnCl₄.5H₂O) was dissolved in ethanol as the precursor solution for the sol. After being mixed with antimony (III) chloride (SbCl₃), a certain amount of CNTs with weight percentage of 1-10 wt % to SnO₂ was dispersed into the former solution by ultrasonic dispersing. The CNTs with diameter from 6 to 8 nm were obtained via catalytic CVD process. The final sol was dip-coated onto a substrate. The as-fabricated sensor samples were dried for the formation of crack-free thin films. Subsequently, the samples were calcined in air at 500°C, the dip-coating and drying operation steps were carried out repeatedly to increase the film thickness (Liu, 2008). Duy el al. (Duy, 2008) also used the solgel process to prepare CNTs-SnO₂-TiO₂ nanocomposite films. The precursors used to fabricate the SnO₂-TiO₂ sol were tetrapropylorthotitanate Ti(OC₃H₇)₄, tinethylhexanoate Sn(OOCC₇H₁₅)₂ and isopropanol C₃H₇OH. To synthesize the CNTs-SnO₂-TiO₂ composite material, the single-walled CNTs (SWCNTs) with a diameter less than 2 nm and MWCNTs with diameters ranging from 20 to 40 nm were introduced and dispersed into the SnO₂-TiO₂ sol solution by an ultrasonic shaker. The film was deposited by spin coating on silica substrate with Pt-interdigitated electrode and was dried at 60 °C and annealed at 500°C. The inclusion of CNTs did not affect the particle size as well as the morphology of the oxides. The sensing properties of those CNTs-oxides sensors towards different ethanol concentrations and operating temperatures were investigated (Duy, 2008). Other sol-gel fabricated CNTs nanocomposite films include SWNTs-SnO2 film for hydrogen detection (Gong, 2004); and MWNTs-SiO₂ for methane, hydrogen and acetylene sensing (Xin, 2005).

Unique properties

CNTs mixed with catalytic metal nanoparticles have been found to significantly improve gas sensing properties of CNTs. The Pt-, Ru- and Ag-CNT nanocomposites prepared by RF magnetron sputtering and PECVD as described previously in Fig. 7 was investigated for NO₂ gas by Penza et al. and the results are shown in Fig. 8. Fig. 8(a) and (b) shows the response curves of those nanocomposite films at a sensing temperature of 25°C and 150°C, respectively.



Fig. 8. (a) Response of CNTs-metal nanocomposite chemiresistors towards NO₂ gas. The thickness of metal-catalyst and CNT layer is 5 nm and 10 μ m, respectively. (b) Time response towards NO₂ gas of the CNT-metal nanocomposite chemiresistors at sensor temperature of 150 °C. (c) Calibration curves, at 150 °C (Penza, 2009).

With comparison to unmodified CNTs, the enhanced response of Pt-, Ru- and Ag nanocluster coated vertically-aligned CNTs layer towards the NO₂ gas was clearly observed at both temperatures as shown in Fig.8 (a) and (b). The minimum gas detection of 0.1 ppm NO₂ was achieved at 150°C for metal coated CNTs. The calibration curves at 150 °C for unmodified and coated CNTs films are shown in Fig. 8(c). The maximum NO₂ gas response was achieved by Ag-coated CNTs. The metal coated CNTs films also significantly enhanced gas detection of H₂, ethanol and toluene up to sub-ppm level that makes metal-CNTs nanocomposites highly promising candidates for environmental air monitoring applications (Penza, 2009). Brahim et al. has also investigated metal-carbon nanotubes (CNTs) nanocomposite materials as the active sensing layer for ethanol vapour detection at room temperature. They found that pure CNTs material was virtually non-responsive at low ethanol concentrations (< 50 ppm), while the metal-CNT composite films (Ti-, Mn-, Fe-, Co-, Pd- or Pt-CNTs) showed extremely high sensitivity to trace ethanol levels with 100-fold or more gains in sensitivity relative to the pure SWNTs (Brahim, 2009).

By mixing semiconductive metal oxides such as SnO₂ with CNTs, the gas sensing properties of the oxides can also be improved. For example, Sb-CNTs-SnO₂ thin film shows higher sensitivity and shorter response time than pure SnO₂ and Sb-SnO₂ thin films for sensing polar gases, such as formaldehyde, ammonia, and toluene as shown in Fig. 9. The figure shows the response of pure oxides and CNTs-oxide nanocomposite films when they were exposed to target gases or dry air alternately. The voltage increased when the target gas was injected and decreased as dry air was introduced. The sensitivity of the Sb-CNTs-SnO₂ thin film is also significantly shorter. CNTs addition was believed to affect the grain growth and surface area of SnO₂ as well as create CNTs-Oxide interfacial region which improves the gas sensing properties (Liu, 2008). CNTs doped SnO₂ film was also investigated by Wisitsoraat et al. (Wisitsoraat, 2006) for ethanol sensing and they found that SnO₂-CNTs nanocomposite can operate with good sensitivity and stability at a relatively low temperature of 250-300 °C.



Fig. 9. Gas sensing response of SnO_2 , Sb-SnO₂ and Sb-CNTs-SnO₂ thin films to (a) formaldehyde, (b) ammonia, (c) benzene, and (d) toluene (Liu, 2008).

The improved gas-sensing properties were attributed to the increasing in surface area of metal oxide induced by CNTs protrusion. The sensitivity to ethanol of CNTs incorporated SnO₂ thin film was found to increase by the factors of 3 to 7 with CNTs inclusion up to 2%. In addition, the response time and recovery time were found to reduce by the factors of 2 or more. However, they also found that if the CNTs concentration is too high, the sensitivity is decreased. Bhuiyan et al. (Bhuiyan, 2008) also observed higher sensitivity and lower operating temperature for SnO₂-SWCNTs nanocomposite films than the pure CNTs or SnO₂ films for the detection of NO and NO₂ gas in the carrier gas nitrogen (N_2) or air. CNTs-SnO₂ films were also investigated by Wisitsoraat et al. (aWisitsoraat, 2007) for sensing ethanol, CO and NO₂, and by Gong et al. for sensing H₂. Wisitsoraat found that 1% CNT-SnO₂ exhibit maximized response to NO₂ with sensitivity of ~10 at NO₂ concentration as low as 250 ppb at 200°C, while Gong found that nanocomposite films have greater sensitivity (a factor of 3), faster response time and recovery time, and less drift in resistance measurement for H_2 sensing. Small amount of CNTs incorporation into SnO₂ proved to be an effective means to enhance gas-sensing sensitivity of semiconductive metal oxide sensors. The improved sensitivity is credited to the large surface to volume ratio of gas sensing film with nano

passes created by CNTs. Other metal oxides that were used to composite with CNTs include SiO₂ and ZnO. Xin et al. (Xin, 2005) found that MWNTs-SiO₂ composite film was sensitive to methane, hydrogen and acetylene while the pure MWNTs was not. They believed that MWNTs and silicon dioxide formed the Schottky junctions. Adsorption of the gas molecules on the surface of the MWNTs affects the space discharge area of the Schottky junction, so that the dielectric constant of nanocomposite films changes with the gas adsorption. ZnO-SWNTs fabricated by oxidizing metallic zinc deposited on a SWNTs template also showed higher sensitivity and lower operating temperature than the zinc oxide film for hydrogen gas sensing (Jung, 2008).

Polymers can also be used to modify CNTs to improve its sensing properties. For example, PMMA-MWCNTs nanocomposite shows fast response and change in resistance upon exposure to different organic vapours. The room temperature gas sensing property of MWCNTs-PMMA nanocomposite makes it very attractive for miniature wireless gas sensor applications. The sensing mechanism of MWCNTs-PMMA films to organic solvents was attributed to the swelling of the polymer matrix due to the absorption of organic vapours which increases the volume and the distance between the nanotubes. The contact resistance between adjacent CNTs thus increases as their distance increase. The extent of swelling and hence the electrical response depends on the solubility of the polymer in the solvent. In addition, CNT surface that contains polar functional groups can also adsorb organic solvent molecules (Abraham, 2004). Hieu et al. investigated the effects of film thickness, annealing temperature, and SWCNTs content on gas-sensing response of PPY-SWCNTs nanocomposite for detection of NH₃ gas at room temperature. They found that the nanocomposite sensor had a response of 26-276% upon exposure to NH₃ gas concentration from 10 to 800 ppm, and their response and recovery times were around 22 and 38 s, respectively (Hieu, 2009). All the above results clearly indicate that by properly mixing metal or metal oxide with CNTs to form nanocomposites, higher sensitivity and lower operating temperature than that of pure metal oxide or CNTs films for gas sensing can be achieved.

5. Conclusion and future directions

Nanocomposite thin film-based gas sensors have been developed and demonstrate huge potential for a variety of applications such as drug, food and environmental monitoring. Different types of nanocomposite thin films can be fabricated by various deposition processes such as PVD, CVD, sol-gel, and other wet-chemical synthesis. It has been proved that the electrical resistance, sensitivity, selectivity, response time and operating temperature of gas sensors can be significantly improved by using nanocomposite films as the active sensing materials. This can be attributed to the complementary behaviours of the consisting materials, the unique interface characteristics and large surface areas, as well as nano-scale dimensional effects. Chemoresistors that measure the resistance change of nanocomposite films as the transducer is the most commonly used sensor structures. Compared to chemoresistors sensors, optical sensors present a number of advantages such as enabling multi-parametric detection, no need for electrical contacts, do not suffer from electromagnetic noise, allow optoelectronic integration and have the potential of multi-gas detection. Optical sensors using SPR response of nanocomposite films that consist of metallic nanoparticles embedded in metal oxide or polymer matrix are of great interest and should be further explored. Acoustic wave sensors are most suitable for polymer based nanocomposites as they can precisely measure the thickness variation when polymers swell after their exposure to the vapours of organic solvents.

Although nanocomposite films have demonstrated their great potential for gas sensor applications, several challenges still remain. Synthesis of nanocomposite films with precisely controlling their chemical composition ratio, micro/nanostructures, phases, surface area and interfacial characteristics is still a challenging task. Depending on the preparation technique and process parameters, the property and behaviours of the nanocomposite sensors can vary significantly; therefore, the ability to reproduce nanocomposite films with consistent properties is very important for their wide use as active sensing materials. Degradation of the nanocomposite films stemming from aggregation of the nanosized components due to relatively strong inter-particle forces between them, micro/nanostructure changes due to high operating temperatures and surface contaminations due to impurity etc. has to be resolved before their large-scale adoption by the industry. With the increased interests and intensive research and development in the field, it is expected that, nanocomposite thin film gas sensors will have a promising future and will make a major impact on the gas sensor industry.

6. References

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Mechanical Alloying: For Formation of Nanocomposite WC/MgO Materials

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1. Introduction

Composites are the combination of two or more materials in which tailored properties are achieved by bringing the combined advantages of both reinforcement and matrix into full play, which gives us a rather high degree of freedom in material design (Zhang et al., 1997). Structurally, reinforcements may be in the form of fibers, particles or whiskers, and recent interest has been attracted on the nanostructured composites (Kalambur & Hall, 1997). Because of the extremely small size of the grains, a large fraction of the atoms in these materials is located in the grain boundaries and thus the composites exhibits enhanced combinations of physical, mechanical and magnetic properties (Koch, 1993; Suryanarayana, 1995; Gleiter, 1989; Suryanarayana & Koch, 1999). Nanocomposites illustrate increased strength, high hardness, extremely high diffusion rates, and consequently reduced sintering times for powder compaction.

Some composites, like WC-Co, have shown an exceptional high value of hardness, and good wear/corrosion resistance. It has been widely used for machining, cutting, wearing, as well as high performance construction and apparatus. However, the process to produce WC-Co is very complicated and costly in the reason that the main component WC is usually obtained by direct synthesis of elemental W and C at high temperature and Co is rare and expensive. Many efforts have been focused on reducing the fabrication cost and finding new materials as the alternative for Co. Fortunately, we have employed a high-energy planetary ball mill to prepare a composite of WC toughened with MgO. The results illustrated that the nanocomposite WC/MgO offered unique combination of high hardness and excellent fracture toughness, which is comparable to the properties of WC-Co. Furthermore, the high-energy planetary ball mill, one kind of mechanical alloying (MA), has been a one-step successful route in synthesizing this compound in powder forms in an inexpensive and faster way.

Mechanical alloying (MA) is a solid-state powder processing techniques involving repeated welding, fracturing and rewelding of powder particles in a high-energy ball mill. MA has now been shown to be capable of synthesizing a variety of equilibrium and non-equilibrium alloy phases starting from blended elemental or prealloyed powders (Benjanmin, 1970; Wright & Wilcox, 1974; Gessinger, 1976; Koch et al, 1983; Schwarz & Koch, 1986; Sherif El-Eskandarany, 1996; Sherif El-Eskandarany et al., 1997). During the past few years, considerable of equilibrium and metastable alloy phases have been synthesized by this simple and inexpensive processing technique – mechanical alloying/milling of metal

powders, including oxide dispersion strengthened materials, supersaturated solid solutions, non-equilibrium crystalline or quasicrystalline intermediate phases and amorphous alloys (Doppiu et al., 2007; Razavi et al., 2008; Legendre et al., 2007).

The present chapter will be a guided introduction to the fabrication of nanocomposites WC/MgO using MA method. The outline of the chapter will be as follows. In Section 2 of this chapter, we will briefly discuss the formation of nanocomposite WC/MgO powders and the mechanism of mechanical alloying at first. This will be followed by a description of the process and process variables. Recent developments in understanding the process of MA through modelling and milling maps are briefly described in Section 2.2, and then the application of artificial neural network (ANN) modelling method in MA process is described. The unique problem of process control agent (PCA) is discussed in Section 2.4. The last Section will present the consolidation of nanocomposite WC/MgO powders.

2. Formation of nanocomposite WC/MgO powders by high-energy planetary ball milling method

Refractory compounds, like WC, are usually synthesized on a commercial scale by direct reduction of metal with the appropriate reactants at high temperatures and pressures. The process is cumbersome, time-consuming and expansive, and the end product is heterogeneous. Mechanical alloying (MA) can be an ideal one-step successful route in synthesizing these compounds. Following is a guided introduction to the details involved in the fabrication of nanocomposite WC/MgO powders *via* MA method.

2.1 Formation of nanocomposite WC/MgO powders and its mechanisms

Reactant mixture powders are commercial powders of WO₃ (1.3 μ m, 99.9 %), graphite (1 μ m, 99.9 %) and Mg (50 μ m, 99.5 %). These powders are mixed at an atomic ratio of 1:1:3. The ball milling experiments are carried out using a QM-1SP4 planetary ball milling machine under argon gas atmosphere. Details of the milling conditions are described in (Zhang et al., 2010). The weight of the powder mixture put into the milling vial is 20g.

The XRD patterns of the mixed powders after milling for different time is showed in Fig. 1. It indicated that the powder milled was a mixture of polycrystalline WO₃, graphite and Mg powders at the initial stage of milling. During high-energy ball milling, the powder particles are repeatedly flattened, cold welded, fractured and rewelded. In this early stages of milling, many new surfaces are created, and they enable the particles to weld together leading to an increase in particle size. Meanwhile, heavy deformation is introduced into the particles. This is manifested by the presence of a variety of crystal defects including dislocations, vacancies, stacking faults, and increased number of grain boundaries. These defect structures enhance the diffusivity of solute elements into the matrix. The composite particles at this stage have a layer structure consisting of various combinations of the starting components (Suryanarayana, 2001).

With further deformation, the particles get work hardened and fractured by a fatigue failure mechanism and/or by the fragmentation of fragile flakes (Suryanarayana, 2004). At this state, the fragments may predominate in reducing the particle size, and the strong agglomerating forces induced by cold welding may be absent. The refined microstructure feature decrease the diffusion distances. Additionally, the slight increase in temperature during milling further helps the diffusion behaviour.

After milling 4.7 h, the diffraction peaks coming from initial elemental powders were no longer visible, and the new diffraction peaks corresponding to WC and MgO phases were detected. When the powder was further milled, the feature of the milled powders XRD patterns did not change. It indicated that a reaction was ignited and finished completely within 4.7 h, leading to the formation of WC and MgO. Thus, the occurrence of the reaction during the ball milling was not gradual but abrupt in a very short milling time. Furthermore, it can be seen that the diffraction peaks were evidently broadened with the increasing of milling time, proving that the milling caused refinement of the particles grains. Consequently, nano-sized WC/MgO powders were obtained after milling for 50 h. This steady-state equilibrium is attained when a balance is achieved between the rate of welding, which increases the particle size, and the rate of fracturing, which decreases the composite particle size.



Fig. 1. The XRD patterns of the mixed powders after milling for different time

From above experimental results, it can be concluded that the oxidation-reduction reaction occurred among WO₃, graphite and Mg by high-energy milling and WC/MgO were formed. The reaction can be supposed as follows:

$$WO_3 + 3Mg \rightarrow W + 3MgO$$
 (1)

$$W + C \rightarrow WC$$
 (2)

where the metal oxide (WO₃) is reduced by a more reactive metal (Mg) to the pure metal (W). The reaction (1) is characterized by a large negative free energy (ΔG =-320kJ) and are therefore thermodynamically feasible at room temperature. The occurrence of the reaction at ambient temperatures is thus limited by kinetic consideration alone.

MA can provide the means to substantially increase the reaction kinetics of the reduction reactions. This is due to the repeated welding and fracturing of powder particles increases

the area of contact between the reactant powder particles which causes a reduction in particle size and allows fresh surfaces to come into contact repeatedly; this allows the reaction to proceed without the necessity for diffusion through the product layer. As a consequence, reactions that normally require high temperatures will occur at lower temperatures during MA without any externally applied heat. In addition, the high defect densities induced by MA accelerate the diffusion process. Alternatively, the particle refinement and consequent reduction in diffusion distances (due to microstructural refinement) can at least reduce the reaction temperatures significantly, even if they do not occur at room temperature.

The high temperature caused by the reaction (1) in the vial expedites the subsequent diffusion reaction of high activity W and C (reaction (2)). The reaction (2) is completed in a very short time. It can be seen from Fig. 1 that all W diffraction peaks disappeared, which is attributed to the diffusion reaction of C particles with W particles in high chemical activity.

In a word, the formation of such composite WC/MgO powders is attributed to the impact energy by high energy ball milling. Due to the impact energy, the superficial activity of Mg and the temperature of local areas increased, which enhanced the reaction between WO₃ and the Mg surface. When this reaction occurs, lots of heat released is enough to form WC between the W and C. From above analysis, it can be concluded that the mechanically induced self-sustained reaction can take place among a mixture of elemental WO₃, graphite and Mg according to reaction (1) and (2) during ball milling and completed in a very short time.

2.2 Modeling studies and milling maps

Generally, the reaction induced by high-energy ball milling can be a self-propagation hightemperature synthesis reaction (SHS) or a gradual diffusion reaction depending on the milling conditions. Different reaction kinetics are attributed to several factors, including thermodynamics, atomic and thermal diffusivity and the mechanical properties of the reactant powders, especially the processing factors such as milling speed, ball-to-powder weight ratio and milling ball diameter. These processing factors will determine the rate of energy transference from milling balls to the powder particles of the processed material. Suryanarayana et al. pointed out that if the energy transferred to powders is rather low, gradual reaction can be the reaction mode, while if it is sufficient high, SHS can be initiated (Suryanarayana et al., 2001).

According to recent studies (Magini & Iasonna, 1995; Magini et al., 1996; Murty et al., 1995; Rojac et al., 2006; Yang et al., 1997), milling maps can be an adaptive method to correlate the milling parameters with the ball milling energy transfer, as well as with the reaction mode. Burgio et al. (Burgio et al., 1991) have derived a set of kinematic equations to estimate the ball-to-powder energy transfer occurring in a single collision event. Magini et al. (Magini et al., 1996) have further studied the collision model, using the energy transfer per impact and the degree of filling for milling maps to the Pd-Si, Fe-Zr and Ti-Al system. Murty et al. (Murty et al., 1995) also have given the milling maps of $Ti_{50}Ni_{50}$ and $Ti_{50}Cu_{50}$ materials, and Rojac et al. (Rojac et al., 2006) have used ball impact energy and cumulative kinetic energy to develop a milling map for NaNbO₃.

Herein, the formation mode of WC/MgO is discussed. The experimental details are described in (Wu et al., 2009). The milling conditions adopted in the study is summarized in Table 1.
Milling speed (rpm)	100	150	200		
Ball-powder weight ratio	5:1	10:1	15:1	20:1	
Number of milling balls	15	30	45	60	
Diameter of milling balls (mm)	10				
Weight of each milling ball (g)	6.67				
Volume of milling vial (ml)	250				
Milling ball/ vial medium	Refractory alloy				
Density of milling ball/vial (kg/m ³)	15×10 ³				

Table 1. The milling conditions adopted in the present study

Fig. 2 shows that the formation mode and the time required for the formation of WC/MgO varied depending on the milling conditions. WC/MgO powders can be synthesized either by SHS or by gradual reaction, and the time required for the formation of WC/MgO (determined from the XRD patterns) in general decreases with the increase in milling speed and ball-to-powder weight ratio.



Fig. 2. XRD patterns of powders milled at different milling speed and ball-to-powder weight ratio for different milling time

All these results can be better understood when considering the energy transfer during milling. Magini et al., Murty et al. and Yang et al. have made some earlier efforts on the proposal of respective milling models (Magini et al., 1996; Murty et al., 1995; Yang et al., 1997). On the basis of these widely used milling models, the energy for the formation of WC/MgO by high-energy ball milling is analyzed, and details are described as follows: The average linear velocity (V_b) and free distance (S) of the milling ball are given by (Yang

The average linear velocity (V_b) and free distance (S) of the milling ball are given by (Yang et al., 1997)

$$V_b = 0.5 \cdot \omega_p \cdot r_0 \tag{3}$$

$$S = 2.228 \cdot r_b \cdot 3 \sqrt{\frac{\rho_b \cdot V_G}{R_{bp} \cdot m_p}} \tag{4}$$

where ω_p is the milling speed of disc, r_0 the radius of the vial, r_b the radius of the milling ball, ρ_b the density of ball, V_G the volume of the vial , R_{bp} the ball-to-powder weight ratio, and m_p the mass of the powder canned in the vial. Then, the collision frequency of each ball can be obtained through the following equation:

$$v = \frac{V_b}{S} \tag{5}$$

The energy transferred per unit of mass can be expressed by (Magini et al., 1996):

$$\frac{\Delta E}{Q_{\text{max}}} = 7.66 \times 10^{-2} \cdot R_p^{1.2} \cdot \rho_b^{0.6} \cdot E^{0.4} \cdot \omega_p^{1.2} \cdot d_b \, / \, \sigma \tag{6}$$

where Q_{max} is the maximum quantity of trapped material, R_p the distance between center of disk and center of vial (R_p =0.115 m), ρ_b , E and d_b is the density, Young modulus and diameter of the milling balls respectively, and σ is the surface density of the covering powder. For refractory ball, ρ_b is 15×10^3 kg/m³ and E is 5.5×10^{11} N/m². By measuring the weight of balls with several interruptions during the milling, σ is estimated to be about 0.25 mg/mm². Please note that the energy is absorbed only by a small quantity of mass trapped in a collision but not by the total powders. We should take all the milling balls into account when considering the influence of ball-to-powder weight ratio. Consequently, the total energy transferred per unit of mass and time can be described by

$$E_b^* = \phi_b \cdot \Delta E \cdot \nu \cdot n_b \tag{7}$$

where n_b is the number of milling balls, ϕ_b is an efficiency factor related to the filling of the vial, which is close to 1 for 1/3 filling of the vial (Magini et al., 1996) and the filling level in the present work is lower than 1/3. Thus Eq. (7) can be rewritten by

$$E_b = \Delta E \cdot v \cdot n_b \tag{8}$$

 E_b is the effective extensive factor. On the hypothesis that all the milling energy is transferred to the powders, the energy accumulation with the increase of milling time (*t*), the milling time request for synthesizing WC/MgO) should be considered, thereby the total energy can be expressed by (Murty et al., 1995)

$$E_t = \frac{E_b \cdot n_b \cdot v \cdot t}{m_p} \tag{9}$$

The above parameters for different milling conditions are calculated and listed in Table 2. To verify Eq. (8), a number of experiments on the WO₃-C-3Mg system have been carried out at various milling speed and ball-to-powder weight ratio. Fig. 3 shows the change of the milling parameters with the different reaction modes. The SHS reaction might occur when the effective intensive factor E_b is over 38.24 kJ g⁻¹ s⁻¹. The WC/MgO can be obtained through the gradual reaction when the E_b is 22.12~38.24 kJ g⁻¹ s⁻¹. No WC/MgO can be

formed when the value of E_b is below 22.12 kJ g⁻¹ s⁻¹. The milling energy maps would be of the prediction for other experiments carried out on the WO₃-C-3Mg system in the different milling conditions.

$\begin{array}{c} \text{Milling} \\ \text{speed} \\ \omega_p \ (\text{rpm}) \end{array}$	Ball- powder weight ratio R _{bp}	Linear velocity V _b (m ·s-1)	Collision frequency v (s-1)	Energy transferred per unit of mass ΔE (J/g hit)	Effective extensive factor E_b (kJ ·g-1 s-1)	Milling Time t (h)	Total energy <i>E_t</i> /10 ⁶ (kJ·g ⁻¹)
	5:1		5.55	51.80	4.31		
100	10:1	0.21	8.81		13.69		
	15:1		9.49		22.12	80	141.58
	20:1		10.08		31.34	60	112.83
	5:1		8.32	84.26	10.52		
150	10:1	0.31	15.13		38.24	35	160.61
	15:1		15.92		60.38	11	53.14
	20:1		16.65		84.18	5.2	26.26
200	5:1	0.42	11.13		19.81	33	156.91
	10:1		22.24	119.00	79.25	6.5	61.82
	15:1		23.09		123.64	4.5	44.51
	20:1		23.91		170.75	2.5	25.61

Table 2. Related parameters calculated at different milling conditions



Fig. 3. Milling map of WC/MgO at different conditions

The relation between effective extensive factor (E_b) and total energy (E_i) can give an idea about the conditions required for gradual reaction and SHS mode during ball milling, as shown in Fig. 4. For WC/MgO synthesized through SHS mode the total energy value required is 25.61~61.82×10⁶ kJ·g⁻¹, and for obtaining WC/MgO through gradual reaction, the total energy value required is above 112.83×10⁶ kJ·g⁻¹, five times more than those powders fabricated with SHS reaction. The big difference in energy value for the two formation mode may be caused by the following reasons:

- 1. For an SHS mode, a small quantity of mixed powders trapped in the collision event could get enough energy to form WC/MgO first. The released combustion heat will be helpful for the following reactions. Therefore, the total milling energy required for the formation of WC/MgO can be maintained at a lower level.
- For a gradual reaction mode, most of the milling energy has been used up in the diffusion process. Moreover, gradual reaction process needs much longer milling time, this means that heat loss is much serious. All the above discussions are based on the present collision model.



Fig. 4. Energy map of WC/MgO synthesized by SHS(●) and gradual (■) reaction

According to above analysis, a conclusion can be easily achieved that nanocomposite WC/MgO powders can be synthesized either by SHS or gradual reaction. In the present work, the milling energy is analyzed by using an improved model on the basis of Magini's and Yang's work, *i.e.* considering the multi-parameters that describe the energetics of the high-energy ball milling process. On the other hand, there still exist some defects, for instance, ignoring the loss of milling energy during which makes the calculated values higher than the actual ones. Whereas, based on the previous hypothesis that the impact energy is entirely absorbed by the powders, the milling maps are provided with predictive capability for choosing the proper milling conditions in the practical high-energy ball milling process.

2.3 Artificial neural network method application in MA process

Owing to the significant scientific and industrial importance of high-energy ball milling, considerable researches have been conducted on the process modeling, as stated previously, mainly based on the mechanistic (Abdellaoui & Gaffet, 1995; D'Incau et al., 2007; Chattopadhyay et al., 2001; Das et al., 1999; Abdellaoui & Gaffet, 1994) and thermodynamic (Badmos & Bhadeshia, 1997; Lu et al., 1997; Suryanarayana et al., 2001) approaches to achieve a great understanding at the atomic and phenomenological level. However, these models cannot be fully and accurately implemented due to the multi-influencing parameters, the inherent complexity and the oversimplified assumptions combined with the highly dynamic, non-linear behavior of a multi-physics and multi-scale nature (Feng, 2004).

Artificial neural network (ANN) is currently one of the most powerful modeling techniques based on a statistical approach, and it is suitable for simulations of correlations which are hard to be described by physical models (Sha & Edwards, 2007). Hence, the ANN technique is ideal for the intricate ball milling processes due to its utility to problems that involve the manipulation of multiple parameters and non-linear interpolation.

ANN provides a mapping of inputs to outputs and consists of computer programs based on the structure of brain. As such, they can be trained to recognize patterns within data. In the human brain, a neuron is a nerve cell which processes incoming information and outputs a signal to the relevant part of the body accordingly. Some inputs are stronger than the others, *i.e.* they are 'weighted'. The total effect of the inputs is the sum of the weighted signals, and, if this exceeds the neuron threshold, a response is produced. By comparison, in an ANN, a number of inputs are applied simultaneously, *via* weighted links, and the node calculates a combined total input. The relation between the input and output is specified by a transfer or activation function, which describes the threshold for deciding on the state of the output of that particular node. A number of nodes may be combined to form a layer, and layers may be interconnected to form a complete network. The detailed procedure of developing the ANN model for the synthesis of nanocomposite WC/MgO powders *via* high-energy ball milling process is described as follows.

2.3.1 Experimental data collection and processing

To develop an ANN with good performance, there needs an adequate quantity of experiment data available. The database was collected through the planetary ball milling experimental results. The experimental procedure is detailed described in (Ma et al., 2009). Constant milling time and atomic ratio of elemental powders were maintained throughout the series of experiments as detailed in previous.

The selection of the input parameters is very important for the ANN modeling. All relevant input parameters must be represented as the input data of the model. Among a number of parameters involved in the ball milling process, the variables, including milling speed (v), ball diameter (d_B) and ball-to-powder weight ratio (R_{BP}) have been chosen as the input parameters. The morphology of the as-milled powders, characterized by crystallite size (d), specific surface area (S) and median particle size (d_{50}) , were the individual output for three separate back-propagation (BP) network models.

In total, 96 input/output data pairs for training the neural network were formed on the basis of the experiments, and the remaining 16 pairs were reserved for testing the performance of the trained network. The ranges of the numerical values of the network

input and output are listed in Table 3. These data was converted and normalized to a suitable form for use with the ANN by

$$v' = \frac{v - \min_{a}}{\max_{a} - \min_{a}} (new \max_{a} - new \min_{a}) + new \min_{a}$$
(10)

where v' is the pattern vector, v is the value of a certain variable (it can be v, d_B or R_{BP} , etc.), max_a and min_a are the maximum and minimum values of the independent variable. Additionally, "1" is its new maximum value (*newmax*_a), and "-1" is the variable's new minimum value (*newmin*_a).

Data	Variable	Values		Moon voluo	Standard doviation	
Data	variable	Maximum	Minimum	Weall value	Standard deviation	
	V(r/min)	350	200	275	64.550	
Input	$d_B (\mathrm{mm})$	10	4	7	2.582	
	R_{BP}	10	4	7	2.582	
Output	<i>d</i> (nm)	35.173	19.876	26.767	4.295	
Output	$S (m^2 g^{-1})$	7.690	0.799	3.791	2.241	
Output	d_{50} (µm)	7.842	0.703	2.276	2.226	

Table 3. Range of the numerical values of the neural network input and output data

2.3.2 Neural network training and its performance

The process of fitting the network to the experimental data is called *training*. During its training phase, the network was repeatedly presented with a set of training patterns, comprising input-output pairs, until either the output error was minimized to a satisfactory level (0.001) or the maximum number of training cycles was reached. On completion of the training, a set of previous unused patterns were applied to the network inputs, here without example outputs. In this way the ability of the network to classify the composites' characteristics on the basis of new information was tested.

The back-propagation (BP) network architecture was selected and applied. It includes an input layer, which just propagates input values to the nodes of the hidden layer, a single hidden layer and an output layer. The employed BP network algorithm is available inside the Neural Network Toolbox (Version 4.0.1), MATLAB® 7.1 (14th release).

In order to determine number of the hidden nodes in the network, several BP networks with various hidden nodes (max to 24 nodes) are considered and the corresponding mean square of the network errors (MSE) are calculated by

$$E(w,B) = \frac{1}{N} \sum_{i=1}^{N} (t_k - a_k)^2$$
(11)

where *N* is the total number of training patterns, t_k is the target/desired value, and a_k is the network output value.

Fig. 5 demonstrates that the number of neurons in the hidden layer for crystallite size model, specific surface area model and median particle size model is 15, 13 and 16 correspondingly, which yield the minimum mean square error for training dataset. As a result, Table 4 lists the specifications of the architecture of the selected neural network.



Fig. 5. Mean square errors of different BP neural networks with different neurons in the hidden layer

Parameters	BP network type	Diagram		
Numbers of input layer	1			
Numbers of hidden layer	1			
Numbers of output layer	1	Input Layer Hidden Layer Output Layer		
Numbers of inputs	3	Dimensionless parameters		
Numbers of neurons in hidden	15	v Ho		
layer for crystallite size		\rightarrow		
Numbers of neurons in hidden	13	d_{B}		
layer for specific surface area		R _{BP} Median particle size		
Numbers of neurons in hidden	16	$\rightarrow O(HO)$		
layer for median particle size				
Numbers of outputs	1			
Activation function	Tangent-sigmoid			

Table 4. Specifications of the BP neural network design

The performance accuracy of the network can be checked by the error of neural network predictions. For the test dataset, neural network predictions are calculated. These are compared with the corresponding experiment values. Thereafter, the relative errors are calculated using

$$Error = \frac{Rm_{EXP} - Rm_{NN}}{Rm_{EXP}} \times 100\%$$
(12)

where Rm_{EXP} is the experimental (measured) crystallite size, specific surface area and median particle size, and Rm_{NN} is the predicted values from the neural network.

The average absolute relative error for the *predictions* of crystallite size, specific surface area and median particle size is 8.22%, 7.88% and 4.05% respectively. They are not too bad, considering the limited amount of training data available and large error prone to X-ray measurements of crystallite size and laser measurement of specific surface area and median particle size. These acceptable performances achieve a result that our BP network model can predict with sufficient accuracy for the practice.

2.3.3 Neural network applications in powder property studies

After the above accuracy evaluation and prediction, the neural network technique can be further applied to the optimization of the ball milling process for fabricating the nanocomposite WC/MgO powders. Fig. 6 shows the response surfaces of powder properties, obtained by BP network models, with the milling parameters. Note that only two ball milling parameters (milling speed and milling ball diameter) are discussed in the present optimization for the reason that the remaining variable (ball-to-powder weight ratio) is mainly affected by the milling time which is maintained as a constant value. According to the research of (Suryanarayana, 2001), ball-to-powder weight ratio can no longer be considered with the certain milling time in the current optimization.



Fig. 6. Surface responses of crystallite size (a), specific surface area (b) and median particle size (c) of the milled powders vs. the milling parameters obtained by ANN technique



Fig. 7. Contour plots of crystallite size (a), specific surface area (b) and median particle size (c) of the milled particles vs. the milling parameters v and d_B

As to the clarification of the response surfaces, the contour plots for those properties are demonstrated in Fig. 7. Variations of the crystallite size, specific surface area and median particle size in the response surfaces could be confirmed with the theories reported by many

other researchers (Suryanarayana, 2001; Calka & Radlinski, 1991; Lai & Lu, 1998; Watanabe et al., 1991). It is widely understood that the faster the mill rotates the higher would be the energy input into the powder. At high milling speeds (or intensity of milling), the temperature of the vial may reach a high value which may be advantageous in the current case where diffusion is required to promote homogenization and/or alloying in the WC powders. Additionally, the size of the grinding medium (milling ball diameter) also has an influence on the milling efficiency. Generally speaking, a large size (and high density) of the milling ball is useful since the larger diameter/weight of the balls will transfer more impact energy to the powder particles.

In a word, the results achieved by the surface responses and contour plots indicate that a consistent agreement exists among the outcomes of ANN modeling, the above theoretical description and the experimental implementation. Therefore, the response surfaces and contour plots can be applied to the optimization of the ball milling process of fabricating the nanocomposite powders. The nanostructured WC/MgO powders posses the excellent morphological characteristics, such as homogeneous shape with fine and smooth surface relief and uniform size (less than 0.8 µm in diameter). These powders will be consolidated into the bulk materials for the further industrial application. On the basis of the contour plots and current experimental circumstances, the optimized milling parameters (300r/min< $v\leq$ 350r/min and 8mm \leq $d_B\leq$ 10mm) can be obtained using this series model of BP neural network.

2.4 Process control agent

As mentioned above, the mechanochemical reaction among WO₃, Mg and C reactant powders to form nanocomposite WC/MgO powders can be the SHS one. However, dangerous explosion caused by SHS may occur abruptly, which is difficult to control. In addition, a significant portion of coarse WC/MgO crystallites and particles may form due to particle melting under the high temperature caused by SHS. Furthermore, the powder yield is low as many particles get adhere to the milling balls and vial, which is difficult to be detached.

There are two possible methods to prevent the combustion reaction and the severe welding, one is to lower the temperature of the milling vial (Jang & Koch, 1990; Guo et al., 1990; Fecht et al., 1990), and the other is to add stearic acid as a process control agent (PCA) to the reactant powders (Suryanarayana & Sundaresan, 1991; Wang et al., 1991). The effects of stearic acid on the ball milling process of CuO-Ca/Ni, Ti-BN and Al-Mg systems had been investigated by Schaffer, Byun and Lu respectively (Schaffer & McGormick, 1990; Byun et al., 2004; Lu & Zhang, 1999). Results show that with the addition of stearic acid, the occurrence of combustion reaction can be successfully delayed or suppressed, the interparticle welding during collisions can be inhibited, and the particle size can be decreased. It may be noted that a combustion reaction should be avoided if one is interested in producing the materials in nanocrystalline state. This is because combustion may result in partial melting and subsequent solidification will lead to the formation of a coarse-grained structure. Another requirement for formation of nanometer-sized particles is that the volume fraction of the by-product phase must be sufficient to prevent particle agglomeration (Suryanarayana, 2001).

The reactant WO₃-Mg-C mixture was charged together with steatic acid (99.9%, flaky) and hard alloy balls (10 mm in diameter) into a hard alloy vial (250 ml in volume). The amount

of stearic acid was controlled from 0 to 2.0 wt. %. More experimental details can be found in (Wu et al., 2010).

2.4.1 Effect of stearic acid on the mechanochemical reaction

As stated above, only the WO₃, Mg and C peaks could be detected in the initial 5 h of ball milling (Fig. 1). When milling for 4.7 h, the WO₃-Mg-C mixture abruptly reacted to form WC/MgO. Slight explosion sound could be heard during milling for 4.7 h, and the temperature of the milling vial reached an evidently high level almost at the same time, as shown in Fig. 8a. These phenomenons indicate that the occurred reaction (1) is a mechanically induced self-propagating reaction. Fig. 8b shows the TEM micrograph for the agglomerated powder which resulted just after the temperature peak. The particles in Fig. 8b are very coarse and most of the size is above 100 nm.



Fig. 8. (a) Temperature vairation of milling vail during milling for reaction (1) and (b) the corrisponding TEM micrograph

The SHS, completes within a very short time, however, it always results in the occurrence of dangerous explosion phenomenon and the formation of coarse WC/MgO particles. With the aim of preventing SHS, stearic acid is added as a PCA. Fig. 9 indicates that the incubation time (the time from the beginning of milling to the occurrence of SHS) for the SHS depends on the concentration of stearic acid. The incubation time is about 5.5 h without stearic acid and there are little changes up to 0.8 wt. % of stearic acid. The addition of stearic acid of between 1.1 and 1.2 wt. % further increases the incubation time, but the SHS still occur. When 1.2 wt. % of stearic acid is added, however, the SHS is suppressed in two experiments while it occurs in another two. With over 1.2 wt. % of stearic acid, reaction (1) always proceeded gradually. Therefore, the critical concentration of stearic acid to inhibit the SHS of reaction (1) is about 1.2 wt. %.

Fig. 10 shows the XRD patterns of the powders with different amounts of stearic acid after 80 h milling. When the concentration of stearic acid is lower than 1.2 wt. %, there is no distinct difference in the XRD patterns of the powders, as shown in Figs. 10a, b and c. However, it can be found from Figs. 10d and 10e that with over 1.2 wt. % of stearic acid, both WC and MgO peaks broaden much more, which means that the suppression of SHS contributed to the reduction of the crystallite size and the increase of mircostrain. The

average crystallite sizes of WC and MgO, estimated by formula in (Chakurov et al., 1987), are 19 and 29 nm without stearic acid, and 10 and 15 nm with 1.4 wt. % of stearic acid respectively, under the same milling conditions. Nevertheless, with over 2.0 wt. % of stearic acid, WC/MgO can't be successfully formed even ball milling for over 100 h, as shown in Figs. 10f and 10g.



Fig. 9. Incubation time for SHS with different amount of stearic acid



Fig. 10. XRD patterns of powders milled for 80 h with (a) 0, (b) 0.8, (c) 1.1, (d) 1.4, (e) 1.8, (f) 2.0 and (g) 2.2 wt.% of stearic acid

The above results indicate that the critical concentration of stearic acid to change reaction (1) from SHS to a gradual reaction is about 1.2 wt. %. In general, the change of reaction mode

by an inert addictive is attributed primarily to two mechanisms, i.e. increasing the heat capacity and decreasing the contact area between the reactants (Takacs, 2002; Chakurov et al., 1987). Munir (Munir, 1988) proposed a simple guideline to decide whether or not a selfpropagating reaction might occur for a certain system. According to his proposal, the reaction can start without additional energy from an exterior source when the adiabatic temperature rise $(-\Delta H/C_p)$ is above 2000 K. The $-\Delta H/C_p$ of reaction (1) calculated from the thermodynamic date will decrease from ~ 6000 K to ~ 5800 K, under which the SHS would still occur. Thus, it seems that the suppression of the SHS by stearic acid is primarily owing to the decrease in contact area among the reactants. The stearic acid, being absorbed on the surface of reactant powders, helps decreasing the contact area among them, which leads to the slowing down of the reaction rate and therefore either delays or completely suppresses the SHS. However, the contact area may be too little to initiate reaction (1), if excessive (>1.8 wt. %) stearic acid absorbed on the surface of reactant powders. It should be noted that such an amount is too small to consider the possibility that change the reaction mode could be induced by other reactions, as there is no other phase can be observed in the XRD patterns, as shown in Fig. 10.

2.4.2 Effect of stearic acid on the microstructure of powders

With the aim to investigate the effect of stearic acid on the microstructure of the mechanical alloyed powders, the powders milled with 0 wt. %, 1.1 wt. %, and 1.4 wt. % of stearic acid for 80 h are characterized by TEM, as shown in Fig. 11. These three powder samples all contain two phases: the first phase WC appears as deep-black grains, while the second phase MgO consists of light-gray grains. Fig. 11a indicates that the crystallite size of WC and MgO milled without stearic acid is rather large and unhomogeneous, in great part are above 50 nm, even approaches to 100 nm. The crystallite size of powders milled with 1.1 wt. % of stearic acid can be a little decreased and its homogeneity of particle size can be slightly improved either, as shown in Fig. 11b. The reaction mode can be changed from SHS to a gradual one when the concentration of stearic acid is increased to be 1.4 wt. %. Fig. 11c shows that there are no such large crystallites and the sizes of the homogeneously distributed WC and MgO crystallites are much smaller, mostly are between 10 and 25 nm. Thus, the average crystallite size and agglomeration can be considerably decreased and the homogeneity of particle size can be obviously improved when the amount of stearic acid is enough to suppress the occurrence of SHS.

During high-energy ball milling process, considerable plastic deformation of powders greatly enhance the surface activity, thus the neighboring powder particles may get together to reduce the surface activity, which can hinder the refinement and mechanical alloying of the processing powders. When an appropriate amount of stearic acid is added into the reactant powders during ball milling, stearic acid will adsorb onto the fresh surface to decrease the surface activity and inhibit the conglomeration of powders, because adsorption is a free energy self-decreasing process. Fig. 11 suggests that the microstructure of powders can be improved with the addition of stearic acid, however, there is no obvious effect unless the amount of stearic acid is enough to change the reaction mode from a SHS to a gradual reaction. This can be expressed by the reason that the vial surface temperature may be maintained at a low level during the synthesis process of WC-MgO through steady gradual reaction, which is in favor of obtaining homogeneously distributed fine particles and crystallites. While the vial surface temperatures may reach a high value due to the excessive

combustion heat liberated during SHS process, and these temperatures lead to the melting, consolidation and formation of large particles of the reaction products.



Fig. 11. TEM pictures of powders milled for 80 h with (a) 0 wt. %, (b) 1.1 wt. %, (c) 1.4 wt. % of stearic acid.

2.4.3 Effect of stearic acid on the powder yield of powders

Powder yield is one of the most important indicators to estimate as-milled powders recovered after ball milling, which is commonly expressed by the ratio between the weight of powders after and before ball milling. Powder yield also can quantificationally reflect the adhering degree of powders during mechanical alloying. Fig. 12 shows the relation between powder yield and the amounts of stearic acid added.



Fig. 12. Relation between powder product yield and the amounts of stearic acid added It can be found by Fig. 12 that the powder yield can be greatly enhanced to be 80.6 % when 1.8 wt. % of stearic acid is added, as other milling parameters are maintained at the same value. After 80h of ball milling, fine WC-MgO powders can be obtained, and both the

surfaces of vial and milling balls are bright and clean, nearly no adhering phenomenon can be observed. On the other hand, the powder yield is rather low (31.5 %) when milled without stearic acid under the same milling conditions. The end powders exhibit with large grain size, and a great quantity of powders get coated onto the surface of the milling balls and vial. While no WC-MgO powders can be formed when over 1.8 wt. % of stearic acid is added, therefore the powder yield under this milling condition haven't been further discussed and investigated.

During ball milling process, constant collisions among milling balls, powders and milling vial result in the plastic deformation of the powders. Small parts of powders get cold welded onto the milling balls and vial, while a great part of powders particles are refined by work-hardening. Due to the increase of the surface activity, the refined powders will be inclined to get together and coated onto the milling balls and vial spontaneously. This is a process in which the free energy gets decreased. Therefore, the adhering of powders to the milling balls and vial is unavoidable when milled without stearic acid. A very thin "protective film" between the powders and the milling balls/vial may form with the addition of stearic acid. This "protective film" prevents the contact between the powders and the milling balls/vial, which decreases the abrasion induced by milling balls, as well as reduces the adhering of powders to the milling media. Moreover, the adsorption of stearic acid on the powder surface can also decrease the surface energy of powder particles, and diminishes the adsorption driving force of powders to the milling balls and vial, consequently reduces the possibility of adhering of powders to the milling balls and vial. As a result, the addition of stearic acid can greatly increase the powder yield, which is an important method to overcome the adhering problem during the process for synthesizing nanocomposite WC/MgO powders.

3. Consolidation of nanocomposite WC/MgO powders

Sintering behavior of nanocomposite WC/MgO powders and its consolidated bulk properties are studied. The as-milled WC/MgO powders were sintered by plasma-activated sintering (PAS) and hot-pressing sintering (HPS) at the same sintering conditions, *i.e.* maximum temperature: 1650 °C, applied pressure: 40 MPa. The microstructures were analyzed and compared in order to understand the influence of the two sintering techniques. The density of the consolidated samples and the following mechanical properties were measured: Vicker hardness and the estimated fracture toughness.

The XRD pattern of the WC/MgO powders and the consolidated sample *via* PAS and HPS method were shown in Fig. 13. The strong diffraction peaks of WC (hexagonal structure) and MgO (cubic structure) were clearly observed. Thus, it indicated the hot-pressing sintered bulk materials were mainly composed of the WC and MgO phases. W₂C phase was detected in the sintered bulk, but its intensity in the HPS sintered sample was greater than those of the PAS one, which may be due to the decarburization phenomena during sintering.

Fig. 14 presents the microstructures of the polished samples sintered by HPS and PAS at 1650 °C. The energy dispersive spectroscope (EDS) analysis reveal that the dispersed white particulates were composed of the Mg and O elements, while the surrounding dark matrix was rich in W and C element. Combined with XRD results (Fig. 13), it is reasonable to

conclude that the composites of WC matrix with the MgO particulates toughened can generally be produced. However, the dispersion states of the toughening particulates were significantly influenced by the sintering method. In the sample sintered by HPS, the MgO showed an irregular polygonal shape and were larger than 2 µm in size (Fig. 14a). Compared with that, the toughening particulates in the bulk consolidated by PAS were presented in a refined and dispersed morphology (Fig. 14b).



Fig. 13. XRD pattern of the end-powders and the consolidated WC/MgO bulk

HPS consolidation of WC/MgO powders resulted in an agglomeration of MgO particulates and pores in the matrix (Fig. 14a), leading to a relatively low bulk densification of 94.56 % theoretical density (T.D.). Sintered by PAS, the refined MgO toughening particulates were homogeneously distributed in the matrix, showing very little aggregation (Fig. 14b). In this instance, a relatively high densification response of 99.3% TD was obtained (Table 5).

Sintering Method	Relative Density/%	Vickers Hardness (HV/GPa)	Fracture Toughness $(K_C/MPa m^{1/2})$	
Hot-pressing sintering (HPS)	94.56	15.43	9.58	
Plasma-activated sintering (PAS)	99.3	17.78	12.21	

Table 5. Some measured mechanical properties of the fabricated bulk materials via HPS and PAS

Table 5 also depicts the hardness and fracture toughness measured on the polished sections. It is clear with the HPS method, the hardness was about 15.43 GPa and the estimated fracture toughness was 9.58 MPa•m^{1/2}. This can be attributed to the pores distribution and significant MgO agglomeration segregation throughout the sintered structure. The hardness of the sample sintered by PAS was measured to be 16.65 GPa, taking the average of at least

10 indentations. The resulting indentation cracks were used as the indication of the fracture toughness (K_c) *via* the model that was suggested by Shetty et al (Shetty et al., 1985). We should note that the Vickers hardness measurements that were made are a rough approximation for the valid K_c test. Hence, they were an approximation of the expected fracture toughness measurements. In a word, the overall mechanical performance of the HPS sintered sample was lower than those of the PAS sintered one. But this indicates the possibility of preparing high-hardness and high-fracture-toughness composite materials.



Fig. 14. Backscattered micrographs of polished surfaces of the samples sintered by (a) HPS and (b) PAS

As stated above, WC/MgO composite can be a new advanced hard refractory material. In Table 6, we provide a comparison of the hardness and fracture toughness values of WC/MgO compacts with those of WC-Co reported by others (Richter & Von Ruthendorf, 1999; Almond & Roebuck, 1988; Kim et al., 2007). It can be seen that the hardness and fracture toughness of WC/MgO is comparable with the value reported in other literatures. The hardness and fracture toughness value of the WC/MgO sample produced by PAS had the highest values, and is as good as the samples with a metallic binder. In contrast to those

microns- and submicrons-grained structure of WC-Co composites, the nanocomposite WC/MgO material has offered unique properties of superior hardness and toughness combination. It is reasonable to propose WC/MgO as a new industrial material.

Reference	Materials	Sintering method	HV (GPa)	<i>K_C</i> (MPa m ^{1/2})
(Richter & Von Ruthendorf , 1999)	WC-10 wt. %Co	PAS	17.64	6
(Almond & Roebuck, 1988)	WC-10 wt. %Co	PAS	13.06	13.5
(Kim et al., 2007)	WC-10 wt. %Co	PAS	17.21	11.6
(Kim et al., 2007)	WC-12 wt. %Co	PAS	17	12.2
This study	WC-MgO	HPS	15.43	9.58
This study	WC-MgO	PAS	17.78	12.21

Table 6. Comparison of mechanical properties of the consolidated WC/MgO bulks and WC-Co with previously reported values

4. Summary

Nanocomposite WC/MgO powders can be successfully synthesized by high-energy planetary ball milling a powder mixture of WO₃, graphite and Mg under room temperature. This technique has a great advantage because it not only overcomes the deficiency of high cost in fabricating WC under high temperature, but replaces the noble metal cobalt with MgO as well.

Studying the mechanism involved in the synthesis, we find that mechanical alloying processing can agitate the reaction mass and continually bring unreacted materials into contact, preventing the products from dividing the reactants separately. This results in a significant increase in reaction rate which provides the occurrence of WC/MgO formation at ambient temperature.

Combined the formation mode with the milling conditions, the milling energy maps for preparing nanocomposite WC/MgO powders by high-energy planetary ball milling are established. Self-propagation high-temperature synthesis reaction (SHS) and gradual reaction are two kinds of formation mode of WC/MgO at different milling conditions. The energy region for gradual reaction and SHS is defined, *i.e.* when the effective extensive factor E_b is above 38.24 kJ g⁻¹ s⁻¹, the reaction mode is SHS; it is the gradual reaction when E_b is 22.12~38.14 kJ g⁻¹ s⁻¹; the formation of WC/MgO cannot be achieved when E_b is below 22.12 kJ g⁻¹ s⁻¹. For SHS, the excessive heat released and high temperature rise during the abruptly occurred reaction make the process difficult to control. The milling energy maps also help to predict capability for fabricating WC/MgO through gradual reaction by adjusting the milling parameters appropriately.

It can be concluded that ball milling is an inherently complex process due to the multiinfluencing parameters. Fortunately, neural network technique (NN) can be the ideal modeling for this highly complicated and non-liner high-energy planetary ball milling process. The BP network is selected since this feed-forward multilayer network is further fully connected. The architecture of the BP network models can be implemented: a) The series model of BP network is designed to be "3-n-1", *i.e.* it includes one input layer which contains the ball milling variables (milling speed, ball-to-powder weight ratio and milling ball diameter), one hidden layers (with different number of nodes [*n*] for different model) and one output layer which indicates the morphological characteristics of the WC/MgO powders (crystallite size, specific surface area and median particle size respectively). b) The tangent-sigmoid function is found to be the transfer activation. c) The number of neurons in the hidden layer (*n*) is 15, 13 and 16 for crystallite size model, specific surface area model and median particle size model individually, which is selected according to the mean square error of BP network calculations. The viability of the model is confirmed by the network prediction errors analysis. The results from the BP network prediction perform a good coherence with the experimental data. Furthermore, the optimization of the ball milling process for fabricating the nanocomposite WC/MgO powder is carried out through the analysis on the evaluated network response surface and contour plots. The optimized milling parameters (300 r/min < $v \le 350$ r/min and 8 mm ≤ $d_B \le 10$ mm) can be obtained through the ANN model and the present experimental details. Accordingly, the BP neural network technique can be applied to the high-energy planetary ball milling process with its high reliable performance and practical significance.

In the course of ball milling, the powder particles may cold-welded to each other due to the heavy plastic deformation among them. The true alloying among powder particles can occur only when a balance is maintained between cold welding and fracturing of particles. Regarding this, a process control agent (PCA) is usually added to the powder mixture during milling to reduce the effect of cold welding. Herein, stearic acid is added as a PCA to the reactant powders. The effects of stearic acid and its amount on the WO₃-Mg-C ball milling process, the microstructure evolutions and powder yield rate of WC/MgO have been investigated. The results show that the crystallite and particle sizes of WC/MgO powders can be refined, the homogeneity of particle size can be improved and the powder yield can be enhanced with the addition of stearic acid as a PCA. Furthermore, the mechanochemical reaction among WO₃, Mg and C reactant powders to form nanocompositie WC/MgO powders can be changed from a SHS mode to a gradual reaction by adding over 1.2 wt. % of stearic acid. The WC/MgO powders synthesized through gradual reaction are possessed of finer crystallites and more homogenous particle size distribution. Compared with the unstable and dangerous SHS, the steady and controllable gradual reaction is more suitable to be applied to the practical production.

The as-milled WC/MgO powders are sintered by plasma-activated sintering (PAS) and hotpressing sintering (HPS) at the temperature of 1650 °C with applied pressure of 40 MPa. The relative density, hardness and fracture toughness of the compacted samples are tested. Results indicate that PAS is an attractive technique that the sintering procedure takes place in a short period of time (consolidation is achieved within a few minutes, 5 minutes). According to the microstructure observation, grain growth of the bulk samples can be minimized and the sintered compacts maintain their unique properties, i.e. superior hardness (HV = 17.78 GPa) and toughness ($K_c = 12.21$ MPa m^{1/2}) combination.

Another important factor in the course of sintering that conquers the grain growth of the bulk samples and uniforms the toughening particulates (MgO) dispersion is the source of the milled WC/MgO powders. When the as-milled WC/MgO powders, which are introduced to the consolidation, have homogeneous shape with fine nanocrystalline grains, the PAS sintering may result in formation of full dense compacts (99 % T. D.). It is worth noting that PAS technique does not form any undesirable reactive products such as W_2C . In conclusion, the composite WC/MgO, which achieves competitive values of hardness and fracture toughness, can be an ideal engineering material as the alternative of WC-Co.

5. References

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Nanocomposite Catalysts for Steam Reforming of Methane and Biofuels: Design and Performance

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1. Introduction

Design of nanocomposite materials with high mixed ionic-electronic conductivity (MIEC) and oxygen mobility possessing a high and stable performance in real operation conditions is now considered as one of the most promising trend in developing new anode materials for IT SOFC (Primdahl & Mogensen, 2002; Atkinson et al., 2004; Wincewicz & Cooper, 2005; Dicks, 1998; Kharton et al, 2006; Marina et al, 1999; Xia & Liu, 2002; Zha et al, 2004; Ishihara et al, 2000) and structured catalysts for steam/autothermal reforming of gas and liquid fuels (Souza & Schmal, 2003; Domine et al., 2008; Sadykov et al., 2009).

State-of-the art Ni/Y₂O₃-ZrO₂ (Ni/YSZ) cermet anodes of solid oxide fuel cells (SOFC) have excellent catalytic properties and stability in the oxidation of hydrogen fuel at SOFC operation conditions (Atkinson et al., 2004). However, the lack of a hydrogen infrastructure and the unsolved hydrogen storage problem have initiated the research aimed at direct utilization of natural gas, which represents one of the key aspects of SOFC technology. Internal steam reforming (SR) is the most promising concept in using the natural gas (as well as bio-gas or bioethanol) as a fuel (Wincewicz & Cooper, 2005; Dicks, 1998). In this case, the reaction takes place directly in the anode compartment, allowing a better management within the stack of heat produced by the exothermic electrochemical oxidation and consumed by the endothermic reforming reaction. Unfortunately, with the Ni/YSZ cermet, coking occurs leading to the deterioration of anode performance (Atkinson et al., 2004; Dicks, 1998). Under high carbon activity environment, Ni metal could also be corroded by the metal dusting. Ni/YSZ cermet anodes can only be used in hydrocarbon fuels if excess steam is present to suppress the carbon deposition, which, however, decreases the electrical efficiency of the cells (Wincewicz & Cooper, 2005; Dicks, 1998). Hence, development of robust anodes with a high and stable activity in the internal reforming of fuels is vital for the natural gas/biogas/bioethanol fuel-based SOFC. Next approaches were suggested up to date to solve this problem:

- Partial or complete replacement of doped zirconia with doped ceria or ceria-zirconia possessing a higher lattice oxygen mobility/reactivity (Atkinson et al., 2004; Wincewicz & Cooper, 2005; Dicks, 1998; Kharton et al, 2006; Marina et al, 1999; Xia & Liu, 2002; Zha et al, 2004; Ishihara et al, 2000). This is combined with partial or complete replacement of Ni by copper (Dongare et al., 2002; Ana et al., 2004). This approach allows not only to prevent coking but also ensures a high performance in SR at intermediate temperatures. In this case, some problems could be caused by considerable chemical expansion of ceria lattice in strongly reducing conditions as well as by copper sintering.
- 2. Replacing doped zirconia by perovskites (mainly, doped La chromites) promoted by metals active in SR (Ni or precious metals, mainly, Ru) (Peña-Martínez et al., 2006; Sfeir et al., 2001; Sauvet & Irvine, 2004; Vernoux et al., 1998; Wan & Goodenough, 2005). In this case, insufficient conductivity of perovskites in reducing conditions could be a problem (Plint et al., 2006).
- 3. Partial or complete replacement of Ni in Ni/YSZ or Ni/perovskite cermets by precious metals (Wan & Goodenough, 2005; Bebelis et al., 2006; Suzuki et al., 1993; Takeguchi et al., 2003). This allows to suppress coking and enhance the middle-temperature performance which is explained by a much higher specific catalytic activity of precious metals in CH₄ SR, Pt being the most active metal (Wei & Iglesia, 2004). In the case of cermets containing only precious metals, apparent drawback is their high cost.

Hence, the most promising approach for achieving a high level of anode activity at middle temperatures in CH_4 steam reforming while preventing coking, keeping a high level of conductivity and a low cost, is to promote Ni/YSZ(ScSZ) cermets by fluorite-like (doped ceria-zirconia) or perovskite-like (mixed chromates-manganites) oxides along with small (~1%) amounts of precious metals (Pt, Pd, Ru). These (nano)composites are comprised of components able to efficiently activate C-H and C-C bonds in the fuel molecules (Ni, precious metals) and oxide components providing activation of water molecules and transfer of hydroxyls and/or hydroxocarbonate/oxygen species to the metal particles where they interact with activated C-H-O species producing syngas (Souza & Schmal, 2003).

In the last years biomass has been recognized as one of the major world renewable energy sources. Bio-oil derived from the fast pyrolysis of biomass or bio-ethanol can be converted via steam reforming into hydrogen or syngas, which can be further used in fuel cells or directed to synthesis of liquid fuels and valuable chemicals (Asadullah et al., 2002). For SOFC, an attractive option is direct internal reforming of bio-fuels on catalytically active anodes (Jamsak et al., 2007). Hence, efficient, inexpensive and robust catalysts for the steam reforming of biofuel are required. The most demanding problem of their design is a heavy coking of catalysts even in the feeds with the excess of steam caused by a high reactivity of bio-fuel components (carboxylic acids, aldehydes, ketones, alcohols etc), thus excluding application of traditional Ni-based steam reforming catalysts, Ni- YSZ anode cermets (Jamsak et al., 2007) or precious metals (Pt, Pd, Ru) supported on alumina, zirconia, etc

(Haryanto et al., 2005; Breen et al., 2002). Hence, inexpensive nanocomposite catalysts on the base of promoted Ni/could be also attractive as active and stable to coking components of catalysts for steam reforming of biofuels.

To ensure a high performance of these composites in steam reforming of a given type of fuel, their composition and preparation procedures are to be properly optimized. Specificity of functional characteristics of nanocomposite materials strongly depends on the properties of interfaces/domain boundaries which could act as paths for fast oxygen diffusion and generate specific surface sites responsible for activation of reagents. Chemical composition and local structure of these interfaces controlling their properties are determined both by the nature of coexisting phases and their interaction depending upon the size of domains, their disordering and nanocomposite synthesis procedure.

This chapter overviews results of research within the frames of a broad international collaboration supported by projects of INTAS, NATO Science for Peace and 6 EC Framework Program aimed at design of nanocomposite active components of catalysts for steam reforming of methane and biofuels into syngas both for the fuel cell application and synfuels production mainly published in last 5 years (Pavlova et al., 2007; Mezentseva et al., 2010; Sadykov et al., 2006c; 2008a,b; 2009a,b,c; 2010a,c; Yaseneva et al., 2008; 29-39). A lot of attention was paid to systematic studies of the effect of chemical composition of doped ceria-zirconia solid solutions on the real structure, oxygen mobility and reactivity in nanocomposites considered to be the most important factors controlling their performance. Information on the basic structural features and oxygen mobility/reactivity in Pt-supported ceria-zirconia solid solutions as well as their catalytic properties in transformation of methane and oxygenates into syngas studied earlier in details (Frolova et al., 2006; Sadovskaya et al, 2007; Sadykov et al., 2006b, 2007a-e, 2009a,d, 2010c) provide required bases for understanding the catalytic properties of nanocomposites constituents.

Nanocomposites possessing promising performance and coking stability in target reactions were supported on anode substrates or heat-conducting metal substrates and successfully tested in realistic conditions in the in-cell methane steam reforming as well as in pilot -scale reactors of CH_4 or oxygenates transformation into syngas.

2. Real structure of (nano)composite materials: Effect of method of preparation on morphology and interaction between phases of composite

To provide compatibility of (nano)composites supported as porous layers on traditional Ni/YSZ cermet anodes (high ionic and electronic conductivity, close values of thermal and chemical expansion coefficients are required), the content of NiO and YSZ in composites is to be rather high. For nanocomposites supported as porous layers on heat-conducting substrates (Crofer interconnects, Ni-Al compressed foam substrates, Fechraloy foils/gauzes covered by protective corundum layer (Sadykov et al., 2008a, 2009c; 2010a), these restrictions are less severe, and the content of NiO and YSZ could be broadly varied as dependent upon the target application.

Hence, next types of (nano)composites were prepared and studied within this research program:

Composite I (specific surface area 11 m²/g) comprised of 60 wt.% NiO+40 wt.% YSZ was prepared by mixing and ball milling of industrial sources followed by calcination at 900 °C for 2 h (Sadykov et al., 2008b). This composite containing rather big particles of NiO and YSZ was promoted by supporting 10 wt.% of fluorite-like (Ce_{0.5}Zr_{0.5}O_{2-x},

 $Pr_{0.3}Ce_{0.35}Zr_{0.35}O_2$, $La_{0.3}Ce_{0.35}Zr_{0.35}O_2$) or perovskite-like ($La_{0.8}Pr_{0.2}Mn_{0.2}Cr_{0.8}O_3$) oxides by impregnation with water solutions of corresponding polyester citric acid-ethylene glycol precursors followed by drying and calcination in air at 700 °C for 4 h.

- 2. Composite II (specific surface area 23 m²/g) comprised of 10 wt.% La_{0.8}Pr_{0.2}Mn_{0.2}Cr_{0.8}O₃+55 wt.% NiO+35 wt.% ScCeSZ was prepared using powdered Sc_{0.1}Ce_{0.01}Zr_{0.89}O_{2-y} electrolyte synthesized by co-precipitation as described elsewhere (Smirnova et al., 2007). ScCeSZ powder was first dispersed in the water solution of Ni nitrate and polyester citric acid-ethylene glycol polymeric precursor of perovskite following so called one-pot synthesis routine (Sadykov et al., 2005b). After evaporation, formed solid residue was decomposed in air at 500°C and then calcined at 700°C for 4 h.
- 3. Composite **III** (specific surface area 9 m²/g) comprised of 60 wt.% NiO+40 wt.% YSZ was prepared by impregnation of powdered $Y_{0.08}Zr_{0.92}O_{2-y}$ (Russian source) with an excess of Ni nitrate solution followed by drying overnight in air at 90°C with subsequent calcination at 800°C. After regrinding, the composite **III** was loaded with 10 wt.% fluorite-like oxides (Pr_xCe_yZr_zO₂, La_qPr_xCe_yZr_zO₂, Sm_qPr_xCe_yZr_zO₂, where y = 0.35, 05; z = 0.35, 0.25, 0.2; x = 0.15-0.3; q = 0.15) by impregnation with respective mixed nitrates solutions followed by drying and calcination at 800 °C (Sadykov et al., 2009b).
- 4. Composite **IV** (specific surface area 28 m²/g) comprised of 10 wt.% $Pr_{0.15}La_{0.15}Ce_{0.35}Zr_{0.35}O_2+55$ wt.% NiO+35 wt.% YSZ (Russian source) was prepared by the one-pot Pechini procedure similar to that used for preparation of composite **II**.
- Composites of series V comprised of 10-80% La_{0.8}Pr_{0.2}Mn_{0.2}Cr_{0.8}O₃+ 90-20% (NiO + YSZ) were prepared by the one-pot Pechini procedure similar to that used for preparation of composite II [38]
- Composites of series VI comprised of 10-80% Sm_{0.15}Pr_{0.15}Ce_{0.35}Zr_{0.35}O₂ + 90-20% (NiO + YSZ) were prepared by the one-pot Pechini procedure similar to that used for preparation of composite II.
- Composites of series VII comprised of 80%Pr_{0.30-x}Sm_xCe_{0.35}Zr_{0.35}O₂ (x=0, 0.15, 0.3) +10%NiO + 10% Y_{0.08}Zr_{0.92}O_{2-x} were prepared by the one-pot Pechini procedure similar to that used for preparation of composite II.

Pd, Pt, Ru or Pt + Ru (0.3-1.4 wt.%) were supported on composites by the incipient wetness impregnation with $PdCl_2$, H_2PtCl_6 or $RuCl_3$ solutions followed by drying and calcinations at 800°C for 2h.

2.1 Microstructural features of (nano)composites by TEM with EDX

2.1.1 Composites with a high content of NiO and YSZ

The initial composite I is comprised of bulky NiO particles and 8YSZ aggregates with a rather good crystallinity without any apparent interaction between these oxide phases (Fig. 1). The perovskite and fluorite phases present on the NiO surface generate a moiré pattern caused by overlapping of complex oxides and NiO lattices (Fig. 2). This suggests rather good epitaxy between these phases due to a strong chemical interaction.

Composite II (Fig. 3) is comprised of loose micron-size aggregates of nanoparticles with pronounced spatial variation of their composition as revealed by EDX. In this system, particles of NiO and perovskite-like phase possessing rather good crystallinity are stacked nearly coherently. In Fig. 4, the interphase boundary a-c corresponds to the ideally matched (100) LnCrMnO₃ and (111) NiO planes, while the boundary b - c corresponds to stacking of (110) LnCrMnO₃ and (002) NiO planes with the angle of distortion equal to 5.38°. A perovskite-like phase is also present as rather disordered regions situated between the NiO particles (Fig. 5).



Fig. 1. Typical image of NiO/8YSZ composite I particles with EDX data



Fig. 2. Typical moire patterns due to perovskite (left) of fluorite (right) layers on NiO particles in composite I.



Fig. 3. Typical TEM image of composite III aggregates with EDX data for regions 1 and 2.



Fig. 4. High resolution image of stacked NiO and perovskite particles in composite III with EDX data for respective regions and DDP from the stacking range. In EDX spectra, CeL subscription refers to the overlapping lines of Ce and Pr.



Fig. 5. TEM image of NiO particles with perovskite inclusions between them (right) and respective EDX spectrum from boundary region (left).

Composite III is comprised of big (~1 mkm) porous aggregates formed by stacking of particles with typical sizes in the range of 10–100 nm (Fig. 6a). YSZ particles are comprised of well-crystallized coherently stacked domains with distances 3.02A° corresponding to the (111) planes of cubic zirconia [JCPDS 70-4431] separated by nanopores with walls oriented along the lattice planes (Fig. 6b). In other regions (Fig. 6c) juxtaposed NiO and fluorite-like oxide particles containing elements corresponding to cations of doped ceria-zirconia oxide are revealed. A high-resolution image of some regions (Fig. 6d) shows nearly coherently intergrown particles of YSZ and NiO. EDX analysis revealed considerable incorporation of components corresponding to 3.08A°. Simultaneously, presence of some Ni in EDX spectrum suggests its presence in the surface layer of YSZ, perhaps, as perovskite-like clusters, though its incorporation into the lattice or nanopores of YSZ is possible as well. Traces of Zr and Y were also revealed in the regions of NiO particles.



Fig. 6. Typical morphology, microstructure and local composition of composite III promoted by Pr-La-Ce-Zr-O and Ru. (a) macro/mesoporous aggregates of particles; (b) disordered nanodomain ZrO2 particle and respective EDX spectrum; (c) disordered nanodomain particles of fluorite-like oxide promoter on the surface of NiO particle and respective EDX spectrum; (d) contact area between NiO and YSZ particle modified by the elements of complex oxide promoter.

2.1.2 Microstructure of composites with a low content of NiO and YSZ

For these composites prepared via Pechini route, big NiO particles are usually not observed (Fig. 7). Hence, in this case Ni cations appear to be mainly incorporated into the surface layer of the main phase –doped ceria-zirconia or mixed chromate-manganite. There is some non-uniformity in phases/elements distribution in nanocomposites as revealed by EDX. Broad variation of (111) spacing in fluorite-like oxide –from 3.08 to 3.13 Å is apparently caused by variation of the chemical composition of neighboring domains.

For composites with a high specific surface area supported precious metals were usually not observed by TEM as separate particles due to their high dispersion and strong interaction with complex oxides.

Hence, TEM and EDX studies revealed pronounced interaction between phases present in composites reflected in redistribution of elements between constituting phases including surface decoration and incorporation into the surface layers and in the bulk of particles. After testing in the reaction of CH₄ steam reforming in stoichiometric steam/methane feeds, NiO particles are transformed into Ni^o. However, majority of particles remain in a close contact with the particles of complex oxide promoters. In this case their surface remains to be free of carbon. Graphite –like deposits were observed only on the surface of Ni particles not covered by complex oxide promoters (Sadykov et al., 2008b).



Fig. 7. TEM images and EDX spectra for nanocomposite 1.2%Pt/80%SmPrCeZr+20Ni/YSZ

2.2 X-ray diffraction data

For composites **I** and **II** with a high content of NiO and doped zirconia, strong reflections of these phases and weak broad reflections corresponding to dispersed complex oxide promoters were observed (Sadykov et al., 2008b, 2009b). After testing in the reaction of CH₄ steam reforming in stoichiometric feeds, NiO is completely reduced to metallic Ni. For composite II without supported Pt group metals, a weak broad reflection at $2\theta \sim 27^{\circ}$ corresponding to graphitized carbon was observed agreeing with TEM data (Sadykov et al., 2008b, 2009b).

More subtle details were revealed in diffraction patterns of composite III and composites with a low content of NiO and YSZ. Thus, for composite III both before and after supporting doped ceria-zirconia oxide, along with reflections corresponding to cubic/tetragonal YSZ phase [JCPDS 70-4431] (highly dispersed c- or t-ZrO₂ phases are not discerned easily by routine XRD analysis (Sadykov et al., 2009b), reflections corresponding to monoclinic zirconia phase [JCPDS 78-1807] were observed as well (Fig. 8). As judged by the ratio of reflections intensity, promotion of NiO + YSZ composite by Pr-La-doped ceriazirconia oxide increases further the content of monoclinic zirconia. This implies that preparation procedure of composite III, namely, successive impregnation of YSZ powder with the excess of acidic nitrate solutions followed by evaporation to dryness and calcination (Sadykov et al., 2009b) favors leaching of Y from doped zirconia. This results in destabilization and disordering of the cubic zirconia structure, while at least the surface layers of perovskite-like yttrium nickelates can be formed. Such variation of the structural features of doped zirconia was not observed for NiO + YSZ (ScCeSZ) composites promoted by complex oxides via impregnation with solutions of polymeric polyester precursor (Pechini route) even for samples with a low content of highly dispersed YSZ (Fig. 9). Hence, acidity of impregnation solutions and the time of their contact with YSZ during evaporation appear to play the main role in leaching of Y from YSZ.

Within all uncertainty of estimation of position for rather broad reflections of dispersed doped ceria-zirconia oxide, it remained more or less the same in nanocomposites as in pure oxides (Fig. 9), so redistribution of elements between YSZ and doped ceria-zirconia particles (if any) can be limited to the interfaces. The broadening of doped ceria-zirconia diffraction peaks in nanocomposite and the intensity decline suggest though some disordering of this phase due to the effect of new incoherent interfaces with NiO and YSZ. Note that reflections of NiO phase are very narrow despite its relatively low amount. Hence, at least for NiO particles observed by XRD, their size distribution is to be rather narrow as well.



Fig. 8. XRD patterns of $Pr_{0.15}La_{0.15}Ce_{0.35}Zr_{0.35}O_2$ (1), 10% $Pr_{0.15}La_{0.15}Ce_{0.35}Zr_{0.35}O_2$ / NiO + YSZ (2) and NiO + YSZ (3). •- $Ce_{0.35}Zr_{0.35}La_{0.15}Pr_{0.15}O_2$, | - $Zr(Y)O_2$ monoclinic, \downarrow - $Zr(Y)O_2$ cubic, \bigvee - NiO.



Fig. 9. XRD patterns of $Zr_{0.92}Y_{0.08}O_2$ calcined at 500 °C (1), $Sm_{0.15}Pr_{0.15}Ce_{0.35}Zr_{0.35}O_2$ complex oxide (2) and composite 80% $Sm_{0.15}Pr_{0.15}Ce_{0.35}Zr_{0.35}O_2/10\%$ NiO/10% $Zr_{0.92}Y_{0.08}O_2$ (3). *- $Zr_{0.92}Y_{0.08}O_2$, +- $Sm_{0.15}Pr_{0.15}Ce_{0.35}Zr_{0.35}O_2$.

For Pt-promoted composites with a low content of NiO, rather narrow reflections corresponding to Pt particles were detected (Fig. 10). As was earlier shown for Pt-supported doped ceria-zirconia nanocrystalline oxides (Sadykov et al., 2007e), only a small part of supported Pt is present as metal particles detected by XRD, while oxidic forms (clusters, Pt²⁺ cations) stabilized due to strong interaction with support dominate. Note that supported Ru is not detected by XRD (Fig. 10) due to a higher stability of its oxidic forms.

Hence, structural studies of nanocomposites comprised of NiO, YSZ, complex oxide promoters and supported Pt group metals revealed pronounced interaction between constituting phases. Decreasing the sizes of constituting phases and modification of preparation procedure favor this interaction manifested as heteroepitaxy, decoration and redistribution of elements between neighboring domains. One-pot Pechini procedure provides the smallest sizes of constituting phases particles, while impregnation with acidic nitrate solutions favor redistribution of elements between phases due to leaching.



Fig. 10. XRD patterns for some composites containing 10%NiO, 10%YSZ and 80% Sm(Pr)CeZrO promoted by 1wt.% Ru (1,2,4), 0.5wt.% Pt + 0.5wt.% Ru (3) or 1wt.% Pt (5).

3. Reactivity of (nano)composites

3.1 H₂ TPR

Reduction of NiO in composites by H₂ proceeds via the topochemical mechanism, which includes generation of Ni^o nuclei at some specific surface sites (outlets of dislocations etc) with their subsequent growth accompanied by the expansion of reaction area at the NiO/Ni^o interface (and, respectively, reaction rate increase) until nuclei overlap forming a dense layer of Ni^o product followed then by the reaction rate decline described by a contracting sphere model (Boldyrev et al., 1979). Hence, this reaction is sensitive to the real/defect structure, dispersion and surface composition of NiO particles in green composites, which are of a great importance for understanding the catalytic properties of these systems in steam reforming of fuels. Oxide additives should not cover all the surface of NiO particles by a dense layer to cause noticeable effect on their reduction characteristics. It is sufficient to decorate a small number of surface defect sites in vicinity of the dislocation outlet or domain/grain boundaries to hamper or accelerate removal of oxygen from these sites, and, hence, dynamics of Ni^o nucleation, thus shifting TPR peak position.

Typical H₂ TPR spectra for NiO-doped zirconia nanocomposites, both initial and with supported complex oxides, are shown in Figs. 11, 12. For all samples, NiO reduction was completed up to 600–700 °C. For composite I, reduction starts at ~280 °C with $T_{max} ~ 350$ °C, which is rather close to typical characteristics for samples of pure NiO or its mechanical mixture with YSZ (Montoya et al., 2000; Sanchez-Sanchez et al., 2007) and agrees with the microstructural data revealing little if any interaction between NiO and YSZ in this case. Supporting Ce–Zr–O oxide on this composite shifts T_{max} to ~400 °C, apparently due to a partial blocking of NiO surface (especially surface defects at which nucleation of Ni° occurs) and/or stabilizing Ni²⁺ cations thus hampering reduction. Indeed, similar position of reduction peak was earlier observed for NiO supported on Ce-Zr-O₂ (Romero-Sarria et al, 2008).



Fig. 11. Typical H₂ TPR spectra for different NiO/YSZ composites promoted by fluorite-like oxides (left) or perovskite-like oxides (right). 5 % H₂ in Ar, 5 l/h, temperature ramp 5°/min. Left: 10% Ce_{0.5}Zr_{0.5}O₂/composite I (1), composite I (2), composite VI (3), 10% SmPrCeZr/composite III (4). Right: 0.3% Pd/10% LaPrMnCr/composite I (1), composite II (2), 0.3% Pd/composite II (3).

For unpromoted NiO + YSZ composite III, reduction starts at ~330 °C and is characterized by three overlapping peaks with T_{max} situated at ~ 350, 400 and 450 °C (Sadykov et al., 2009b). In addition, the high-temperature (up to 700°C) tail of hydrogen consumption was observed for both undoped and doped samples of composite III. The first peak can be assigned to reduction of NiO particles not modified by interaction with YSZ. The second peak is close by position to that in composite I promoted by Ce_{0.5}Zr_{0.5}O₂ oxide (Fig. 11), so it can be similarly explained by decoration of the surface of NiO particles with irreducible $Y(Zr)O_x$ oxidic species. Indeed, TPR peaks with T_{max} situated even at higher (450–600°C) temperatures were observed in the case of NiO supported on zirconia, ceria-zirconia or alumina (Montoya et al., 2000; Srinivas et al., 2003; Matsumura & Nakamori, 2004). By analogy with these data, the high-temperature tail of hydrogen consumption can be assigned to reduction of Ni cations incorporated into the bulk of doped zirconia particles (vide supra). Hence, TPR data revealed pronounced variation of the reactivity of NiO particles/species even in unpromoted NiO + YSZ composites, which could reflect different degree of chemical interaction between components.

Supporting doped ceria-zirconia complex oxides on composite III practically eliminates the first TPR peak situated at \sim 350°C (Fig. 11), slightly shifts the second peak to higher temperatures and increases the relative share of the high -temperature peak at \sim 470°C. A high-temperature reduction tail remains to be observed for all samples. This implies that the second impregnation provides modification of the surface of all NiO particles present in composite by Zr and rare-earth cations.

For composite VI prepared via Pechini route with the same type of PrSmCeZrO complex oxide additive and having much smaller content of NiO and YSZ only one H₂ TPR peak (Fig. 11, curve 3) was observed. A lower intensity of this peak as compared with that for other samples (curves 1 and 4, Fig. 11) correlates with a smaller NiO content, while its position is rather close to that for other peaks assigned to reduction of NiO particles decorated by fluorite-like oxides. This suggests that reactivity and lattice oxygen mobility of small NiO particles strongly interacting with complex fluorite-like is rather close to that of bulky particles decorated with fragments of fluorite-like oxides.

Complex perovskite oxide strongly hampers NiO reduction in the composite I (Fig. 11, curve 1): reduction peak shifts to ~460°C even despite co-promotion with Pd. This is explained by the relatively low reducibility/lattice oxygen mobility of complex manganochromite (Peña-Martínez et al., 2006; Sfeir et al., 2001; Sauvet & Irvine, 2004) rather uniformly covering the surface of NiO particles in this composite thus hampering reduction. For composite II also containing complex perovskite phase as an additive and prepared via one-pot Pechini route, the reduction peak is shifted to even higher (~530°C) temperatures (Fig. 11, curve 2). In agreement with TEM data (vide supra) this suggests even stronger interaction between the perovskite and NiO particles in this sample. Appearance of the high-temperature shoulder at ~600°C implies that some Ni cations could be even incorporated into the bulk of perovskite particles/domains thus forming Ni-substituted oxide (Sauvet & Irvine, 2004; Sfeir et al., 2001). Promotion of this composite with a small amount of Pd shifts reduction peak to lower temperatures and removes high-temperature shoulder (Fig. 11, curve 3).

In general, promoting effect of supported Pt group metals on the oxides reduction by hydrogen is a well-documented phenomenon explained by the efficient activation of H₂ molecules on the metal particles and spill-over of atomic hydrogen onto the oxide surface, thus easily removing reactive oxygen forms (Bernal et al., 2002). Downward shift of H₂ TPR peak is observed for any mechanism of the solid oxide reduction, either topochemical (such as NiO reduction) or diffusion-controlled (reduction of ceria-zirconia solid oxide solution). Facilitation of the lattice oxygen mobility due to incorporation of precious metals into domain boundaries and subsurface layers is demonstrated as well (Sadovskaya et al., 2007).

Promotion of composites by Ru or Pt clearly accelerates their bulk reduction by hydrogen (Figs. 12) characterized by the main peak situated at 370-400°C. In addition, in the lowtemperature (100-300°C) range, new peaks appear apparently corresponding to reduction of different Ru and/or Pt oxidic species accompanied by reduction of complex fluoritelike oxides. For Ru supported on ceria or zirconia, peaks assigned to reduction of RuO₂ species with different dispersion are situated at 80-100°C [Hosokawa et al., 2003; Yan et al., 2007). For Pt-supported Pr-Ce-Zr-O samples, reduction starts at $\sim 150^{\circ}$ C with the main maximum situated at ~ 280°C and a shoulder at ~ 200°C (Sadykov et al., 2007e). Hence, TPR peaks at 115-150°C observed for Ru-promoted samples of composites with a high NiO/YSZ content (Sadykov et al., 2009b) suggest rather weak interaction of RuOx species with other phases present in composites. When Ru cations are incorporated into the surface vacancies of La-Sr-chromate with the perovskite structure, these peaks are shifted to higher (180-200°C) temperatures (Yan et al., 2007). Hence, peak observed at ~200°C for nanocomposite with a high (80%) content of Pr-Ce-Zr-O fluorite can be assigned to reduction of RuO_x species strongly interacting with this oxide, perhaps, modified also by dissolved Ni cations (Fig. 12).

This interaction apparently facilitates reduction of NiO present in promoted composites, since T_{max} of the main reduction peak is shifted downward. For Pt-supported nanocomposite (Fig. 12), position and shape of the low-temperature peak is practically the same as that observed for Pt/Pr-Ce-Zr-O samples (Sadykov et al., 2007e). Intermediate position is observed for Pt+Ru-promoted samples (Fig. 12) suggesting formation of mixed PtRuOx oxidic species.



Fig. 12. H₂ TPR spectra of 80%Pr_{0.3}Ce_{0.35}Zr_{0.35} +10NiO+10YSZ composite (1) promoted with 1wt.%Pt (2), 1wt.% Ru (3) or 0.5wt.% Pt + 0.5wt.% Ru (4)

3.1 TPR by fuel molecules (CH₄, C₂H₅OH) and reoxidation by H₂O

Temperature-programmed reduction of composites by fuels (methane, ethanol) followed by reoxidation with H₂O characterizes mobility and reactivity of oxygen species and provides also an additional information on ability of surface sites to activate reagents.

3.1.1 CH₄ TPR

Reduction of bulk NiO sample (a starting compound for preparation of composite I) starts at ~400°C and occurs in a narrow (~100°C) temperature range with practically simultaneous appearance of deep (CO₂, H₂O) and partial (CO, H₂) oxidation products (Fig. 13). While CO₂ evolution rapidly falls to zero, other products are observed up to 800°C. H₂ evolution declines to zero when sample is completely reduced. This means that bulk Ni⁰ particles are not able to continuously dissociate CH₄, aparently due to a rapid surface blocking by the graphitic carbon.



Fig. 13. Typical CH₄ TPR data for NiO (left) and nanocomposite **III** (right). Experimental parameters for Figs. 13-14: contact time 0.1 s, 1% CH₄ in He, temperature ramp 5° /min.

For undoped composites, reduction by CH_4 starts at higher than for pure NiO temperatures (Fig. 13), which agrees with H_2 TPR data (vide supra) and is explained by migration of irreducible cations from YSZ onto the surface of NiO. Some H_2 evolution continues even after complete reduction of composites due to CH_4 decomposition. This suggests that interaction between components even in undoped composites prevents formation of a dense layer of graphitic carbon.

Doping by complex oxides and Pt group metals facilitates the reduction shifting TPR peaks to lower temperatures (Fig. 14). This is explained by a higher efficiency of Pt group metals in C-H bond dissociation as compared with the centers of NiO or fluorite-like/perovskite-like oxides. Indeed, reduction of doped ceria or ceria-zirconia oxides by methane starts from \sim 400°C with evolution of deep oxidation products followed by syngas generation at higher (>700°C) temperatures (Sadykov et al., 2007a). As far as CH₄ pyrolysis is concerned, there appears to be some synergy between the action of Pt group metal, complex oxide additive and Ni. Hence, interaction between components in nanocomposite apparently helps to prevent formation of dense graphitic layers in the course of CH₄ pyrolysis. Polymerized $C_xH_vO_z$ species inevitably formed on the surface of nanocomposites due to this pyrolysis appear to possess more loose structure due to incorporation of oxygen atoms. Reoxidation of deposited coke by H₂O revealed that for Pt-supported doped ceria-zirconia sample CO₂ evolution in the course of H₂O oxidation starts at temperatures below 400°C without any evolution of H_2 up to ~ 550°C (Fig. 15). It clearly can be explained only by decomposition of some surface carbonate complexes -either organic ones within coke precursors or inorganic ones. The maximum of CO, CO_2 and H_2 evolution due to oxidation of coke by water accompanied by simultaneous reoxidation of doped ceria--zirconia is situated at ~ 880°C (Fig. 15). For Ni/YSZ composites, both promoted or not, oxidation of deposited during CH4 TPR runs carbonaceous species accompanied by simultaneous CO₂, CO and H₂ evolution starts earlier and proceeds faster than for Pt-supported fluorite-like oxides (Fig. 15). This suggests involvement of Ni surface atoms together with Pt in gasification of the surface coke. Indeed, while Ni atoms can be oxidized by H₂O producing hydrogen and oxygen atoms, it is impossible for Pt atoms. So, the function of Ni in this case is to provide efficient activation of mild oxidant- water at temperatures lower than those typical for reduced doped ceria-zirconia oxide. On the other hand, Pt atoms could use these oxygen atoms supplied to them via spillover for the efficient oxidation of coke precursors.



Fig. 14. Typical CH₄ TPR data for samples of $1.4Pt/10Pr_{0.15}Sm_{0.15}Ce_{0.5}Zr_{0.2}O_2/composite III (left) and <math>1Ru/10LaMnCrPr/compositeV$.
Another new feature revealed in these experiments is evolution of CH_x (or, in general, hydrocarbons) in the process of H₂O TPO of reduced and coked promoted composite (Fig. 15). This supports hypothesis that complex oxide promoters make deposited coke species less dense and, perhaps, containing a bigger fraction of hydrogen atoms (Sadykov et al., 2008b), so they are more easily cracked by interaction with the surface hydroxyls.

In H₂O TPO spectra of both promoted and unpromoted composites (Fig. 15) peaks of CO₂ evolution in the isothermal mode at 880°C are present. A similar by position peak is present in the H₂O TPO spectrum of Pt-supported coked doped ceria-zirconia oxides (Fig. 15, left). Hence, its appearance in the case of nanocomposites TPO spectra can be explained by oxidation of a part of carbonaceous species located on the surface of YSZ or doped ceria-zirconia particles remote from the interface with Ni particles.

3.1.2 C₂H₅OH TPR

In these experiments, to prevent condensation of unreacted ethanol and its partial oxidation products in the gas analyzer, a cooled to -40°C trap was situated at the reactor exit. This precludes estimation of carbon balance and degree of ethanol conversion. However, analysis of dynamics of products evolution allows to make useful conclusions about reactivity and route of transformation of ethanol for different types of composites.

Figs. 15, 16 show typical results of ethanol TPR experiments for composites with broadly varying compositions. In general, their reactivity with respect to ethanol is comparable: at ~ 300° C H₂ appears followed by other products including H₂O, CO₂, CO and CH_x. While CO₂ and H₂O are products of ethanol oxidation by the lattice oxygen of composites, CH_x is comprised of non-condensed products passed through the trap such as CH₄ and C₂H₄ formed due to cracking and dehydration of ethanol (de Lima et al., 2008). After complete reduction of catalysts, evolution of H₂ and CO continues due to decomposition of ethanol (Domine et al., 2008). Though it is inevitably accompanied by accumulation of surface carbonaceous species, however, within the time scale of experiments, performance is stable which suggests deposition of loose coke species. Since in all cases at the steady state the H₂/CO ratio in the products is close to 2.5, by stoichiometry of ethanol decomposition this coke should retain a lot of hydrogen atoms. CH_x formation due to ethanol cracking continues only in the case of composites containing doped ceria-zirconia oxides (Fig. 15, left). In studied conditions concentrations of CO (~0.5-0.75%) and H₂ (~ 1.25-1.75%) were rather close for studied composites.

Temperature-programmed reoxidation by H_2O of deposited carbonaceous species starts at rather low (~ 400°C) temperatures and proceeds fast (Fig. 16). Hence, for nanocomposites containing even relatively low content of complex oxide promoters carbonaceous deposits derived from ethanol are highly reactive, which is one of the criteria of stability of these composites performance in steam reforming of ethanol (de Lima et al., 2008).

4. Catalytic activity in SR of CH₄ and biofuels

4.1 Catalytic properties of dispersed nanocomposites in methane steam reforming 4.1.1 Composites with fluorite-like oxide additives.

Typical values of CH₄ conversions for different nanocomposites and estimated from these values effective first-order rate constants are given in Figs. 17, 18 and Table 1.



Fig. 15a. Temperature-programmed oxidation by H_2O of reduced and coked in CH_4 TPR runs samples of 1.4 wt.% $Pt/Pr_{0.15}Sm_{0.15}Ce_{0.5}Zr_{0.2}O_2$ (left) and 1.4 wt.% $Pt/Pr_{0.15}Sm_{0.15}Ce_{0.5}Zr_{0.2}O_2$ / composite III (right) samples. 1% H_2O in He, 5°/min, 0.1 s.



Fig. 15b. Typical EtOH TPR spectrum for sample of nanocomposite series **VI** promoted with 80%SmPrCeZr (left) and nanocomposite series **V** promoted by 80%LaPrMnCr (right). Experimental conditions for Figs. 15-16: 1% EtOH in He, contact time 0.1 s, temperature ramp 5° /min.



Fig. 16. EtOH TPR (left) followed by H_2O TPO (right) for nanocomposite series **V** promoted by 1%Ru and 10%LaPrMnCr.



Fig. 17. Temperature dependence of CH₄ conversion (left) and effective first-order rate constants (right) for different composites at 10 ms contact time. Left: 1-10 wt.% $Pr_{0.3}Ce_{0.35}Zr_{0.35}O_2/composite$ **III**, 2-1.3 wt.% Ru/10 wt.% $Pr_{0.15}La_{0.15}Ce_{0.35}Zr_{0.35}O_2/composite$ **III**, 3-0.3 wt.% Pt/10 wt.% $Pr_{0.3}Ce_{0.35}Zr_{0.35}O_2/composite$ **I**, 4- composite **IV**. Feed 8% CH₄+ 8% H₂O in Ar. Right: 1-composite **I**, 2-Ce_{0.5}Zr_{0.5}O_2/composite **I**, 3-0.3%Pd/10%Ce_{0.5}Zr_{0.5}O_2/composite **I**, 4,5-0.3%Pt/10% $Pr_{0.3}Ce_{0.35}Zr_{0.35}O_2/composite$ **I**. Feed 8% CH₄+ 8% H₂O (1-4) or 8% CH₄+ 24% H₂O (5).

Supporting complex ceria-zirconia oxides increases catalysts performance at temperatures exceeding 600°C and stabilizes it at high temperatures (Figs. 17, Table 1) apparently due to hampering of coking. Some samples based upon fluorite oxides promoted composite **III** remain inactive at 650°C (Table 1), while composite **IV** demonstrates a good performance starting already from 550°C (Fig. 17). This can be explained both by a higher specific surface area of composite **IV** as well as by a higher degree of interaction between components of this composite provided by one-pot Pechini route of synthesis, and, hence, stabilization of small active Ni clusters on the surface of oxidic components of composite (vide supra).

For the stoichiometric feed, Pd as co-promoter further increases performance of ceriazirconia promoted composite I (Fig. 17, Table 1) making it highly active even at temperatures below 600°C. Pt as co-promoter also ensures a high activity in the middletemperature range (Fig. 17, Table 1). Indeed, at 650°C, effective first –order rate constants estimated for the plug-flow reactor are as high as 30-40 s⁻¹ (Fig. 17). Hence, more efficient activation of CH_4 molecules on Pt or Pd clusters demonstrated by CH_4 TPR experiments allows to increase the overall performance of Ni-containing catalysts in the intermediate temperature range, while dispersed fluorite-like oxide promoter along with Ni apparently plays the major role in activation of water molecules and transfer of activated oxygencontaining species (hydroxyls, hydroxocarbonates) to the sites where activated CH_x species are located, thus preventing formation of coke.

The performance of samples co-promoted with Pt and fluorite-like oxides tends to increase in feeds with the excess of steam (Figs. 17, Table 1). This is important from the practical point of view since in real SOFC operation conditions, the oxygen ions transfer through the cell increases the overall content of oxidants within the porous composite anode. The increase of steam content in the feed increases the rate of activated hydrocarbons species transformation into syngas, thus preventing the surface coking and ensuring a high performance of composite co-promoted with Pt and fluorite-like oxide. For Pt as a copromoter, the effect of the steam excess in feed strongly depends on the exact chemical

Composition	CH ₄ conversion, %	
$CH_4: H_2O$	1:1	1:3
Ce _{0.5} Zr _{0.5} O ₂ /composite I	23	
$1.4 \text{ wt\% Pt}/\text{La}_{0.3}Ce_{0.35}Zr_{0.35}O_2$	15	14
0.3 wt.% Pd/Ce _{0.5} Zr _{0.5} O ₂ /composite I	43	0
0.3 wt% Pt/La _{0.3} Ce _{0.35} Zr _{0.35} O ₂ /composite I	30	26
$0.3 \text{ wt.} \% \text{ Pt/Pr}_{0.3}\text{Ce}_{0.35}\text{Zr}_{0.35}\text{O}_2/\text{composite I}$	35	50
1.03 wt.% Pt/Pr _{0.3} Ce _{0.35} Zr _{0.35} O ₂ /composite I	0	52
0.5 wt.% Ru/Pr _{0.3} Ce _{0.35} Zr _{0.35} O ₂ /composite I	12	24
0.3 wt.% Pd/LaMnCrPr/composite I	26	12
1 wt.% Ru/LaMnCrPr/composite I	70	
Pr _{0.3} Ce _{0.35} Zr _{0.35} O ₂ /composite III	0	
1 wt.% Ru/Pr _{0.3} Ce _{0.35} Zr _{0.35} O ₂ /composite III	32	
1 wt.% Ru/Pr _{0.15} La _{0.15} Ce _{0.35} Zr _{0.35} O ₂ /composite III	36	
1 wt.% Ru /Pr _{0.15} Sm _{0.15} Ce _{0.5} Zr _{0.2} O ₂ /composite III	19	
Composite IV ($10Pr_{0.15}La_{0.15}Ce_{0.35}Zr_{0.35}O_2 + 55NiO + 35YSZ$)	40	
Composite V_1 10LaPrMnCr+90Ni/YSZ (4.1 m ² /g)	21	
Composite V_2 50LaPrMnCr+50Ni/YSZ (8.1 m ² /g)	20	
Composite V_3 80LaPrMnCr+20Ni/YSZ (12 m ² /g)	22	
1% Ru/composite V_1 (3 m ² /g)	70	
1% Ru/composite V_2 (8.9 m ² /g)	45	32
1% Ru/composite V_3 (6.2 m ² /g)	18	
0.7 % Ru/composite V_2		72*

Table 1. Values of CH₄ conversion for CH₄ SR at 650°C on composites promoted with fluorite/perovskite-like oxides and Pt, Pd or Ru. 10 ms contact time,; 1:1 feed (8% CH₄+ 8% H₂O in He), 1:3 feed (8% CH₄+ 24% H₂O in He) and 1:2 feed* (20% CH₄ + 40% H₂O, Ar balance).

composition of the oxide additive. Thus, for sample co-promoted with La-Ce-Zr-O oxide, the effect of the steam excess is small, while for combination of Pt with Pr-Ce-Zr-O oxide additive, this effect is well pronounced (Fig. 17, Table 1).

Note also that for Pt-supported fluorite-like oxides without Ni addition performance is independent upon the water excess (Table 1). A non-additive increase of performance due to supporting Pt along with fluorite-like oxides on Ni-containing composite (a synergetic effect) is thus apparent.

For Pd supported on a composite promoted by ceria-zirconia, the increase of steam content in the feed suppresses the low-temperature performance (Table 1), which could be explained by stabilization of less reactive oxidized Pd species by fluorite-like oxide. Here the main role is played by a higher stability of Pd oxidic forms (perhaps, some surface phases including both Pd and Ce cations) as compared with those of Pt. A lower ability of oxidized Pd species to activate methane is thus responsible for a low activity in feeds with the steam excess.

For Ru as a co-promoter of composite I in combination with the fluorite-like oxides, the excess of steam also positively affects the low-temperature performance (Table 1). However, this performance is lower than for Pt-containing samples in all feeds, so Pt is more efficient co-promoter than Ru in combination with complex fluorite-like oxides. This can be explained by a higher efficiency of Pt in activation of methane (Wei & Iglesia, 2004).

For samples promoted by the same amount of Pt, activity is also higher for sample with a higher Ni content despite a lower specific surface area. Hence, the efficiency of the composite in CH₄ SR is defined by the content of components (Ni, Ru, Pt) activating fuel molecules. On the other hand, when Pt or Pd are supported on Ni/YSZ composite without oxide additives, methane conversion is not improved (Sadykov et al, 2006c). This suggests that namely combination of precious metals with oxide promoters helps to provide enhanced activity of composites in the intermediate temperature range. Due to a low content of supported precious metals, their effect can be assigned to modification of some specific defect centers of Ni particles. This suggestion agrees with a high performance of composite **IY** prepared via one-pot Pechini synthesis procedure (Fig. 17) even without promotion by precious metals.

The synergy of the catalytic action of components in nanocomposites is retained for feeds with the excess of steam. Thus, for nanocomposites containing Pt and SmPrCeZr as copromoters, sample with a higher Ni content provides significantly higher CH₄ conversion in the whole temperature range in both stoichiometric (1:1) and more oxidizing (1:3) feeds (Fig. 18). At a low Ni content, the excess of steam provides a higher CH₄ conversion in the whole temperature range due to efficient activation of CH₄ on Pt sites remaining in the metallic state even in the oxidizing conditions. At a high Ni content, a complex temperature – dependent effect of the steam excess on activity suggests interplay of several factors determined by interaction between Pt, Ni and fluorite-like oxide and affecting efficiency of CH4 and H₂O activation and, hence, steady-state oxidation degree of Ni surface and its coverage by coke.



Fig. 18. Effect of water excess in the feed on performance of nanocomposites promoted by Pt and SmPrCeZr (left) or Ru and LaPrMnCr (right) in)) in CH₄SR an H₂O/CH₄ =1 (a) or 3(b). Contact time 10 ms, CH₄ concentration 8%. Left: 1-Pt/10SmPrCeZr/Ni/YSZ, 2-Pt/80SmPrCeZr/Ni/YSZ. Right: 1- Ru/50LaPrMnCr/Ni/YSZ, 2- 50LaPrMnCr/Ni/YSZ.

4.1.2 Composites with perovskite-like oxide additives

Ni/ScCeSZ cermet without oxide promoters was not able to provide a steady-state performance in the methane SR in stoichiometric feeds due to very fast coking leading finally to the reactor plugging (Sadykov et al., 2006c, 2008b). After reduction by H_2 , composite II comprised of Ni/ScCeSZ cermet promoted by perovskite-like oxide demonstrates a reasonably high and stable activity at temperatures exceeding 650°C (Sadykov et al., 2008b). Similarly, promotion of composite I by perovskite oxide allows to obtain a reasonable

performance in methane steam reforming even at 650 °C (Table 1). By itself, La-Pr-Mn-Cr-O perovskite is inactive in SR of methane. However, incorporation of Ni cations into the lattice of such irreducible perovskites provides a reasonable level of activity in methane steam reforming (Sauvet & Irvine, 2004). Hence, observed high and stable activity of perovskitepromoted composites in CH₄ SR in stoichiometric feed can be explained by a partial dissolution of NiO in the acidic polyester solution at the preparation stage. At subsequent calcination, Ni-containing perovskite is formed (vide supra EDX data). Under contact with reducing reaction media, small highly reactive Ni clusters are segregated on the surface of perovskite oxide being stabilized by interaction with this matrix stable in reducing conditions. In addition, the surface of big NiO particles in non-reduced composite is covered by the perovskite layers (vide supra). Hence, big Ni⁰ particles generated due to NiO reduction in the reaction media are decorated by perovskite-like oxidic species. A high efficiency of these species and/or separate perovskite particles in activation of steam and carbon dioxide facilitates gasification of CH_x species produced by methane activation on Ni, thus preventing coking. This level of high-temperature activity for perovskite-promoted composite I (Table 1) is close to that provided by ceria-zirconia oxide promoter. Hence, similar factors affecting surface properties of Ni particles in promoted composites as well as enhanced activation of water and/or CO₂ molecules on the surface sites of oxide additives could operate in the case of both types of oxide promoters ensuring high and stable performance of composites in methane SR in stoichiometric feeds, especially at rather high (>700°C) temperatures.

The increase of steam/methane ratio from 1 to 3 was found to decrease the high – temperature performance of perovskite-promoted composite I (Sadykov et al., 2006c, 2008b). This can be assigned to partial oxidation of Ni surface atoms contacting with perovskite species/particles and their stabilization as less active perovskite-like fragments.

Co-promotion of composites with perovskite-like oxide and Ru allowed to achieve a high level of middle-temperature activity in feeds with different steam/methane ratios (Table 1, Fig. 18). For composite **II**, the increase of Ru content from 0.3 to 1 wt.% decreases activity in the stoichiometric feed and increases it in the feed with the excess of steam (Sadykov et al., 2010b). This behavior can be explained by a higher rate of CH₄ activation on the surface of sample with a higher Ru content, thus leading to deactivation due to coking in stoichiometric feed. In a feed with the excess of steam, enhanced rate of activated CH_x species gasification prevents coking and provides a higher performance of sample with a higher Ru content due to a higher rate of CH₄ activation. Similar features observed for composite **I** co-promoted with fluorite-like oxide and Pt (Table 1) agree with this explanations of the precious metal content and feed composition effects.

For composites series V containing LaPrMnCr and promoted by 1%Ru (Table 1), activity increases with Ni content, thus clearly demonstrating synergy of Ni+ Ru action due to suppression of coking ability of Ni sites explained by the surface alloys formation. Activation of H_2O molecules on Ni atoms can be important as well.

As follows from Fig. 18, Ni/YSZ cermet promoted only by perovskite –like complex oxide provides the same CH₄ conversion in both types of feed, while co-promoting effect of Ru is much stronger in the stoichiometric feed. This suggests that in feed with the steam excess Ru is in part transformed into less active oxidic forms stabilized by perovskite-like complex oxide.

When comparing two series of samples co-promoted with precious metals and either fluorite-like or perovskite-like oxides (Table 1), the middle-temperature performance of the best samples of both series is comparable. For samples promoted with perovskite-like oxide,

the highest activity is provided by supporting Ru, while for samples with fluorite-like oxide additives, the highest performance is observed after loading Pt. Hence, these two types of systems can be considered as promising for the practical application. In general, a better performance is provided by YSZ-containing catalysts (Sadykov et al., 2010b). Though more detailed studies are required for elucidating the exact role played by the rare-earth cations in determining catalytic properties of these nanocomposites, it is clear that observed trends are not determined by the oxygen mobility in doped zirconia particles which is higher for ScCeSZ (Smirnova et al., 2007).

Hence, the most efficient promoter for Ni/YSZ -based composite catalyst is Pr(Sm)-doped ceria-zirconia in combination with Pt. Since Pt is more expensive than Ru, the latter was also used as a co-promoter in combination with either perovskite or fluorite oxide when supporting thin layers of NiO+YSZ-based nanocomposites on different substrates (vide infra).

As far as the preparation procedures are concerned, one-pot Pechini route apparently provides the highest activity of promoted composites, at least, for systems with complex fluorite-like oxide additives. Hence, this method was selected as a basic one for preparation of dispersed promoted composites for subsequent supporting on different substrates. As follows from Fig. 19, performance of nanocomposite active components prepared via this route is sufficiently stable in feeds with a small excess of steam.

Temperature-programmed oxidation of nanocomposite samples discharged from reactor after testing in stoichiometric feeds demonstrated that combined action of precious metals and complex oxides decreases the amount of deposited carbon providing thus high and stable performance (Sadykov et al., 2006c, 2008b).



Fig. 19. Stability test for nanocomposite 10%Sm_{0.15}Pr_{0.15}Ce_{0.35}Zr_{0.35}+ 55%NiO+35%YSZ +1.4%Pt at 600 °C, feed 20% CH₄ + 40% H₂O, Ar balance, contact time 60 ms.

4.2 Catalytic properties of dispersed nanocomposites in ethanol steam reforming

In this reaction, in general, in the middle-temperature range, activity of all composites, promoted by Ru or not, was rather high (Table 2, Fig. 20). This is explained by a high activity of Ni in this reaction provided coking of its surface is hindered by oxidic promoters. Moreover, specific activity of Ni supported on alumina is reported to be even higher than that of low-loaded Ru (Fatsikostas et al., 2002; Haryanto et al., 2005; Sanchez-Sanchez et al., 2007). This agrees with the results of Srinivas et al. (Srinivas et al., 2003) demonstrating a

high and stable activity in ESR of composites comprised of 40wt. % NiO and 60 wt.% CeO2 (CeO₂-ZrO₂) prepared via hydrothermal route. Hence, promoted nanocomposites efficient and stable in steam reforming of methane are also quite promising for the steam reforming of ethanol. As can be inferred from the hydrogen content in converted feed, at 700 °C, even at short contact time, up to 70% of ethanol is converted along the steam reforming route. $C_{2}H_{4}$ and CH_{4} were not revealed in the products, while they were inevitably present for catalysts comprised of precious metals supported on alumina (Erdőhelyi et al., 2006; Romero-Sarria et al., 2008). Hence, for developed composites containing YSZ and complex fluorite-oxide promoters, primary route of ethanol transformation into syngas apparently does not include ethanol dehydration or cracking. This agrees with very high CO₂/CO ratio in products at 700 °C in diluted feed clearly not conforming to the equilibrium composition of converted feed (Erdőhelyi et al., 2006; Romero-Sarria et al., 2008) or to results obtained with a high content of ethanol in the feed (vide infra). Absence or very low concentration of CO in products for composites promoted by oxides with a high Ce content (Table 2) implies that red-ox properties of promoters are also responsible for routes of ethanol transformation into carbon oxides (Erdőhelyi et al., 2006; Vargas et al., 2005). Since at high temperatures acetates are the only surface species detected by infra-red spectroscopy (Erdőhelvi et al., 2006), at short contact times CO_2 can be considered as primary product of their transformation. Since CH₄ was not observed in products, this transformation is not simple cracking usually accompanied by CH₄ formation, but should include interaction of ethoxide species with reactive hydroxyls or hydroxocarbonate species.

N⁰	Sample	Products concentration. %		
		СО	CO ₂	H ₂
1	$10\% Pr_{0.15}Sm_{0.15}Ce_{0.35}Zr_{0.35}O_2+55\%$	0.1	0.4	1.1
	NiO+35%YSZ			
2	$80\% Pr_{0.15}Sm_{0.15}Ce_{0.35}Zr_{0.35}O_2 + 10\%$	0.1	0.4	1.1
	NiO+10%YSZ			
3	50%LaPrMnCr+30%NiO+20%YSZ	0.1	0.4	1.0
4	80%LaPrMnCr+10%NiO+10%YSZ	0.1	0.4	1.1
5	10%Pr _{0.3} Ce _{0.35} Zr _{0.35} O ₂ +90%NiO/YSZ	0.1	0.5	1.7
6	1%Ru/10%Pr _{0.3} Ce _{0.35} Zr _{0.35} O ₂ +90%NiO/YSZ	0.2	0.4	1.5
7	10%Pr _{0.25} Ce _{0.5} Zr _{0.25} O ₂ +90%NiO/YSZ	0	0.5	1.8
8	1%Ru/ $10%$ Pr _{0.25} Ce _{0.5} Zr _{0.25} O ₂ +90%NiO/YSZ	0	0.5	1.9
9	$10\% Pr_{0.15}La_{0.15}Ce_{0.35}Zr_{0.35}O_2+90\% NiO/YSZ$	0.1	0.3	1.3
10	1%Ru/ $10%$ Pr _{0.15} La _{0.15} Ce _{0.35} Zr _{0.35} O ₂ +90%NiO/YSZ	0.3	0.4	1.4
11	10%Pr _{0.15} La _{0.15} Ce _{0.5} Zr _{0.2} O ₂ +90%NiO/YSZ	0.1	0.3	1.1
12	Ru/10%Pr _{0.15} La _{0.15} Ce _{0.5} Zr _{0.2} O ₂ +90%NiO/YSZ	0.1	0.3	1.2
13	10%Pr _{0.15} Sm _{0.15} Ce _{0.35} Zr _{0.35} O ₂ +90%NiO/YSZ	0.1	0.3	2.0
14	Ru/10%Pr _{0.15} Sm _{0.15} Ce _{0.35} Zr _{0.35} O ₂ +90%NiO/YSZ	0	0.5	1.9
15	$10\% Pr_{0.15}Sm_{0.15}Ce_{0.5}Zr_{0.2}O_2+90\% NiO/YSZ$	0	0.5	1.9
16	Ru/10%Pr _{0.15} Sm _{0.15} Ce _{0.5} Zr _{0.2} O ₂ +90%NiO/YSZ	0	0.5	1.9

Table 2. Concentrations of products (H₂, CO and CO₂) in the ethanol steam reforming at 700 °C for different composites prepared by modified Pechini method (1-4) and by impregnation (combinatorial) rout (4-16). Contact time 0.036s, feed composition 0.5% C₂H₅OH + 2.5% H₂O in He.



Fig. 20. Rates of products formation in ethanol steam reforming at 700 °C on nanocomposites. Contact time 36ms, feed 0.5% EtOH + 2.4%H₂O in He. 1-10%SmPrCeZr+55%NiO+35%YSZ, 2-80% SmPrCeZr +10%NiO +10%YSZ, 3-50%LaMnCrPr+30%NiO+20%YSZ, 4-80%LaMnCrPr +10%NiO+10%YSZ

Some variation of performance with nanocomposites composition and preparation route is worth commenting. For samples based on composite **III** prepared via successive impregnation, the lowest performance was demonstrated by nanocomposites containing $Pr_{0.15}La_{0.15}Ce_{0.7-x}Zr_xO_2$ (Table 2). This clearly correlates with the highest temperatures of H₂ TPR peaks for these samples (Sadykov et al., 2009b) reflecting their lower reducibility, and, hence, a lower mobility and reactivity of lattice oxygen due to stabilizing effect of a big basic La cation. Since in diluted ethanol+ water feeds the catalysts were tested after pretreatment in O₂, this correlation can be explained either by insufficient reduction of Ni in La-containing catalysts, or by a lower mobility and reactivity of surface hydroxyls/hydroxocarbonates bound with big La cation. The latter can result in the surface coking decreasing performance. Indeed, for nanocomposite promoted by $Pr_{0.15}La_{0.15}Ce_{0.5}Zr_{0.2}O_2$ with the lowest hydrogen concentration in products (Table 2), TPO oxidation after reaction revealed accumulation of up to 18 monolayers of carbonaceous deposits on the surface.

Effect of supporting Ru on promoted composite **III** strongly depends upon the composition of complex oxides (Table 2). For PrSmCeZr- promoted composites possessing a high activity, supporting Ru slightly decreases hydrogen yield. For composite promoted by $Pr_{0.15}Sm_{0.15}Ce_{0.35}Zr_{0.35}O_2$, co-promotion with Ru increases CO₂ yield but decreased CO and H₂ yield. Hence, at short contact times and in diluted feeds, water gas shift reaction is apparently not equilibrated.

When Ru was supported on less active composites promoted by La-containing oxides, another effects were observed: both hydrogen and CO_x yields were increased. While the increase of CO yield can be assigned to acceleration of reverse water gas shift reaction catalyzed by Ru particles weakly interacting with promoting fluorite-like oxides in these composites (vide supra), increase of hydrogen and CO_2 content in the feed suggests that the overall transformation of ethanol along the steam reforming route is accelerated as well, perhaps, due to decreasing the surface coking and/or accelerating other stages of intermediates (acetate etc) transformation into hydrogen and carbon oxides.

For SmPrCeZrO-promoted nanocomposites prepared via one-pot Pechini route (sample 1, Table 2) performance is lower than for nanocomposites of the same composition prepared via consecutive impregnation (sample 13, Table 2). This demonstrates that nanocomposite

microstructure affected by the preparation route plays important role in performance of these catalysts in steam reforming of ethanol.

The decrease of Ni content in nanocomposite from 55 to 10% only moderately decreased performance (Table 2), which can be explained by a higher dispersion of Ni (vide supra).

Nanocomposites promoted by LaPrMnCrO perovskite and prepared via Pechini route demonstrate a higher activity in ethanol steam reforming than catalysts promoted by doped ceria-zirconia oxides and prepared by the same method (Table 2, Fig. 20). Since the trend was usually reversed for CH₄ steam reforming, such a simple explanation as a higher dispersion of Ni more easily incorporated into the perovskite structure could be not sufficient. Perhaps, for ethanol steam reforming presence of red-ox cations such as Mn which can be involved in H₂O activation along with Ni (vide supra) can be important as well.

4.3 Catalytic performance of nanocomposites supported on structured substrates

For supporting thin layers of nanocomposites, Ni/YSZ anode plates, Ni-Al foam substrates as well as thin-foil or gauze Fechraloy substrates were used.

The Fecralloy gauze substrate (woven from the wires with diameter 0.2 mm and ca. 0.2 mm spacing) was first precovered by a thin (ca. 5–10 microns) corundum sublayer by blast dusting technique (Ulyanitskii et al., 2006) followed by washcoating with La-stabilized γ -Al₂O₃ (3.6 wt.%) from an appropriate suspension followed by calcination under air at 1100°C for 2 h. Before supporting active components, the gauze was cut into square pieces to be stacked with Ni-Al foam plates.

Composite powders synthesized via one-pot Pechini route (vide supra) were ultrasonically dispersed in isopropyl alcohol with addition of polyvinyl butyral as a binder to make a slurry. Thin layers of composites were supported on heat-conducting substrates using these slurries and slip casting or painting procedures followed by drying and calcination at 1100°C after each supporting step until loading of 4-7 wt.% was achieved. Ru or Pt were supported by the incipient wetness impregnation followed by drying and calcination under air at 800°C.

Catalytic performance of monolithic catalysts with nanocomposite active components on different substrates in the reaction of natural gas and ethanol steam reforming in concentrated feeds was studied in the stainless steel flow reactors equipped with external heating coils (Sadykov et al., 2010a) using a pilot-scale installation (feed rate up to 1 m³/h). Water and ethanol were supplied by a pump and sprayed via a nozzle into a specially designed monolithic Fechralloy honeycomb evaporation/mixing unit heated by passing the electric current (Sadykov et al., 2009a). Reagents and products concentrations were analyzed by GC.

Fig. 21 compares methane conversions for different plate-like structural elements in stoichiometric steam/methane feed with supported layers of nanocomposite containing fluorite-like oxide promoter and Ru. While at temperatures below 550°C the initial Ni/YSZ anode substrate is not active, supporting composite layers on all substrates provides a reasonable activity in the low-temperature range. Activity of these layers on different substrates is comparable, which agrees with reasonably high intrinsic activity of nanocomposite active components (vide supra). This allows to use these structural elements for in-cell steam reforming of methane to provide an efficient heat management. A high activity of unpromoted Ni/YSZ anode platelet manufactured by the Research Center of Jülich (Germany) at temperatures exceeding 600°C is worth noting as well. In this case, as judged by the carbon balance, a slow coke accumulation in stoichiometric feed takes place which is to deactivate anode sooner or later.



Fig. 21. Temperature dependence of CH₄ conversion on catalytic platelets of 1x2 cm² size. 8 % CH₄+8% H₂O in He, contact time 25 ms. Left: 1%Ru/Pr_{0.3}Ce_{0.35}Zr_{0.35}O₂/Ni/YSZ layers on Ni/YSZ anode platelet (1) foam Ni-Al substrate (2) and Crofer interconnect (3). 4-unpromoted Ni/YSZ anode platelet. Right: 0.5%Ru/La_{0.8}Pr_{0.2}Mn_{0.2}Cr_{0.8}O₃/Ni/YSZ (1) and 0.5%Ru/Pr_{0.3}Ce_{0.35}Zr_{0.35}O₂ Ni/YSZ (2) layers on Ni/YSZ anode substrate.

When nanocomposite layers supported on different substrates contain as co-promoters Ru and perovskite-like oxide, performance is better than for combination of Ru and fluorite-like oxide (Fig. 21), following similar trend for powdered samples (vide supra). Combination of Pt with fluorite-like oxide as co-promoters in supported nanocomposite layers on different substrates also provides a high and stable activity in methane steam reforming even in feeds with higher (20%) concentration of methane close to realistic composition (Fig. 22).



Fig. 22. Conversion of CH₄ (1,2) and H₂ concentration in converted dry feed (3,4) for CH₄ steam reforming on nanocomposite Pt/Pr_{0.3}Ce_{0.35}Zr_{0.35}O₂/Ni/YSZ layers supported on one side of Ni/YSZ anode platelet (1,3) or porous Ni-Al substrate (2,4). CH₄/H₂0/Ar = 20/20/60. Contact time 25 ms.

As follows from both optical and SEM images after stability tests (Fig. 23), supported nanocomposite layer retains its integrity without any cracks or detachment from the underlying anode substrate despite transformation of NiO into Ni in composite as well as in the anode substrate in the reaction conditions. This is provided by a close composition of both substrate and supported layers ensuring matching of chemical and thermal coefficients of shrinkage/expansion. Developed porosity of supported layers helps to avoid diffusion limitations for rather fast CH₄ SR reaction.



Fig. 23. Optical image (left, x50) and SEM image (right) of Ni/YSZ anode platelet with supported nanocomposite layer after stability tests.

In addition to the direct in-cell steam reforming of methane occurring on catalytically active anodes of SOFC, nanocomposite catalysts supported on heat-conducting substrates such as Crofer interconnects or foam Ni-Al alloy can be efficiently applied for so called indirect incell steam reforming of methane within the anode compartment of a stack (in fuel channels etc) (Dicks, 1998). In this case, the effect of the oxygen transfer across the cell under load is of much less importance, so selection of active components can be primary oriented on achieving the highest performance in feeds with steam/methane ratio close to stoichiometry and its stability.

For the indirect in-cell reforming of methane on separate structural elements comprised of nanocomposite active components supported on heat –conducting metal alloy substrates, the problem of thermal expansion compatibility with substrates is less crucial as compared with that for porous nanocomposite layers on anode platelets. Hence, content of Ni in active component can be decreased to improve its resistance to sintering and coking. On the other side, decreasing Ni content could decrease catalytic activity, especially in feeds with the water excess (vide supra).

Systematic studies of the effect of Ni content in nanocomposite active component on their performance revealed that the best compromise is achieved at Ni content in the nanocomposite with YSZ and complex promoting perovskite-like or fluorite-like oxides around 25% (NiO content in green nanocomposite 30 wt.%). As demonstrated in Fig. 24, in this case the active component provides required level of activity and on-stream stability when tested both as a fraction and as a porous layer supported onto foam Ni-Al substrate. Note that the temperature dependence of conversion is practically identical for the fraction and platelet. Hence, mass and heat transfer effects are indeed negligible for this type of substrate.

To check the effect of up-scaling the size of structured catalysts on their performance in the reaction of methane steam reforming, a package comprised of stacked foam platelets and gauzes was tested in concentrated natural gas/steam feeds.

For the stack comprised of either of 3 Ni-Al foam plates (Fig. 25) or 12 Ni-Al-foam plates and 11 sheets of Fecralloy gauzes loaded with $La_{0.8}Pr_{0.2}Mn_{0.2}Cr_{0.8}O_3$ + NiO + YSZ + Ru active component (Fig. 26), hydrogen concentration in the effluent was nearly identical at the same temperature and contact time. This means that heat and mass transfer does not affect strongly performance of these structured catalysts, which is rather good providing >45% H₂ in the effluent.



Fig. 24. Temperature dependence of CH₄ conversion (left) and its variation with time-onstream at 600 °C (right) for 0.25 mm fraction of nanocomposite **V** +0.7Ru (1), and 1x2 cm² Ni-Al platelet with supported active component (2, 3). Loading 5.3 wt. % nanocomposite **V** +0.85 wt.% Ru (2) or 3.8 wt. % nanocomposite **V** +0.47 wt.% Ru (3). Contact time 10 ms for (1), 25 ms for (2, 3) and 50 ms for testing stability with time-on-stream. Feed composition 20% CH₄ +40% H₂O, Ar balance.



Fig. 25. Effect of temperature (left) and contact time (STP) at 600° C (right) on concentration of components in effluent for steam reforming of natural gas on stack of 3 plates 40x40x1 mm³ each. Feed composition 35% of natural gas + 60% H₂O + 5%N₂; contact time 0.15 s at 600° C or 0.5 s at STP (left).

Tests for 100 h with start-up and shut-down of pilot installation each day (8 hours working time per day) confirmed stability of this level of H_2 content in effluent (Fig. 26).

The same package of 12 Ni-Al-foam plates and 11 sheets of Fecralloy gauzes loaded with $La_{0.8}Pr_{0.2}Mn_{0.2}Cr_{0.8}O_3 + NiO + YSZ + Ru$ active component was used for oxysteam reforming of ethanol in pilot installation. In this process performance was also stable providing a high concentration of hydrogen (Fig. 27). The increase of steam excess in the feed helps to increase the hydrogen yield by increasing ethanol conversion as well as by decreasing content of such by-products as methane and ethylene.



Fig. 26. Temperature dependence of H₂ and CO content in effluent (left) and stability tests at 630°C (right) for the reaction of natural gas (NG) steam reforming on a stack comprised of 12 Ni-Al-foam plates and 11 sheets of Fecralloy gauzes loaded with $La_{0.8}Pr_{0.2}Mn_{0.2}Cr_{0.8}O_3 + NiO + YSZ + Ru$ (volume 34x34x34 mm³). Feed 33% NG + H₂O (H₂O/C = 1.9) in Ar, contact time 0.15 s. Time between probes 2 h, package was cooled and warmed in steam each day.



Fig. 27. Concentration of products in the effluent stream of ethanol oxysteam reforming on stack comprised of 12 Ni-Al-foam plates and 11 sheets of Fecralloy gauzes loaded with $La_{0.8}Pr_{0.2}Mn_{0.2}Cr_{0.8}O_3 + NiO + YSZ + Ru$ (volume 34x34x34 mm³). Feed composition: 5% O2+ H₂O +25% EtOH + N₂. T inlet 700°C, contact time 0.3 s.

5. Kinetic analysis of methane steam reforming on anode structural elements

The kinetics of the methane–steam reaction is based upon a 13-step mechanism of H_2 ; CO and CO₂ formation with three rate determining steps (Xu & Froment, 1989). Three reversible macrosteps are as follows:

• Steam reforming (SR)

$$CH_4 + H_2O \leftrightarrow 3H_2 + CO \qquad \Delta_r H_{298 K} = 206.2 \text{ kJ mol}^{-1}$$
(1)

• Water-gas shift (WGS)

$$CO + H_2O \leftrightarrow CO_2 + H_2 \qquad \Delta_r H_{298 \text{ K}} = -41.2 \text{ kJ mol}^{-1}$$
(2)

• *Complex shift reaction (SSR)*

$$CH_4 + 2H_2O \leftrightarrow 4H_2 + CO_2 \qquad \Delta_r H_{298 K} = 165 \text{ kJ mol}^{-1}$$
 (3)

Kinetic parameters of these steps were estimated by analyses of experimental data obtained in a slot-like reactor for the nanocomposite platelet with size 1x2 cm² loaded with 5.3% wt.% of nanocomposite 50%LaMnPr+30%NiO+20% YSZ promoted by 0.85 wt.% Ru. The power law rate equations for the reactions (1) - (3) were expressed in the general form:

$$R_{i,r} \left[kgmol \cdot m^{-1} \cdot s \right] = k_{f,r} \prod_{j=1}^{N_r} \left[C_{j,r} \right]^{\eta'_{j,r}} - k_{b,r} \prod_{j=1}^{N_r} \left[C_{j,r} \right]^{\eta'_{j,r}} ,$$

where Arhenius parameters for forward reaction rate constants are written in the form: $k_{f,r} = A_r T^{\alpha_r} \exp\left(-\frac{E_r}{RT}\right).$

Here, N_r is number of chemical species in the overall molecular reaction r (SR, WGS, and SSR); C_{j,r} is molar concentration of each reactant and product species j in reaction r (kgmol/m³); $\eta_{j,r}^{'}$ is forward rate exponent for each reactant and product species j in reaction r, $\eta_{j,r}^{'}$ is backward rate exponent for each reactant and product species j in reaction r. The backward rate constant for reaction r, $k_{b,r}$, were computed from the forward rate constant using the following relation: $k_{b,r} = \frac{k_{f,r}}{K_{eq,r}}$, where $K_{eq,r}$ is the equilibrium constants for the three main reactions (1)- (3) respectively:

$$\begin{split} K_{eq,SR}\left[atm^{2}\right] &= \frac{p_{CO}p_{H_{2}}^{3}}{p_{CH_{4}}p_{H_{2}O}} = \exp\left(-\frac{\Delta G_{SR}}{RT}\right),\\ K_{eq,WGS}\left[atm^{0}\right] &= \frac{p_{CO_{2}}p_{H_{2}}}{p_{CH_{4}}p_{H_{2}O}} = \exp\left(-\frac{\Delta G_{WGS}}{RT}\right),\\ K_{eq,SSR}\left[atm^{2}\right] &= \frac{p_{CO}p_{H_{2}}^{4}}{p_{CH_{4}}p_{H_{2}O}^{2}} = \exp\left(-\frac{\Delta G_{SSR}}{RT}\right). \end{split}$$

Respective values of effective kinetic parameters for the reactions (1) - (3) obtained by fitting the experimental data are given in Table 3.

The fixed conversion temperature dependences were analyzed with the developed rate equations (Table 3).

	$A_{f,r}$	α_r	$E_{f,r}, J / mol$
$r_{SR} = k_{f,SR} C_{CH_4} C_{H_2O}^2 - k_{b,SR} C_{H_2}^{0.25} C_{CO}$	4.5×10^{4}	-2.65	125000
$r_{WGS} = k_{f,WGS} C_{CO}^{0.85} C_{H_2O}^{0.65} - k_{b,WGS} C_{CO_2}$	2.4×10^2	0	42000
$r_{SSR} = k_{f,SSR} C_{CH_4} C_{H_2O}^{1.25} - k_{b,SSR} C_{H_2} C_{CO_2}$	38	0	81000

Table 3. Kinetic parameters of the rates of three basic macrosteps for the catalytic platelet loaded with nanocomposite active component.

To perform numerical experiments a steady state plug-flow reactor model describing the change of each reaction component along the catalytic platelet is written in the differential form:

$$\frac{d\left(uc_{i}\right)}{dl} = S_{sp} \sum_{j=1}^{3} V_{ij} r_{j}$$

$$\tag{4}$$

Here, c_i is concentration of i-component in mol/m³, u – superficial velocity of gas mixture through the reactor (m/s), S_{sp} - specific surface area, (m⁻¹), v_{ij} -stoichiometric coefficients; r_j -reaction rate for the three global reactions (mol*m-2*s-1), expressed in the empirical form of the power law rate kinetics for the global reactions (1)-(3) as as $r_j = \frac{R_j}{c^*}$, where S*- active

surface area (m²/kg). A second-order Rozenbroke algorithm with an automatic choice of the integration interval was used to solve the set of equations. The Fortran computed code was developed to implement the described algorithm. The predictions based on the kinetic models with the parameters summarised in Table 3 were compared with the experimental data (Fig. 28). A good agreement demonstrates that the *power* law model is *able* to predict with certainty the reaction behavior within the temperature region 600-700°C, which is of special interest in the case of in-cell methane reforming for intermediate temperature solid oxide fuel cells.

The same model was applied to analysis of experimental data on the natural gas steam reforming over stack comprised of three parallel Ni-Al platelets (50x50x1 mm) loaded with the same nanocomposite active component and separated by 1 mm gaps. In these experiments operational temperature, the feed linear velocity and the steam-to-natural gas ratio were varied. A comparison of simulated and experimental data obtained for this stack has been performed by using kinetic parameters estimated for one small platelet (Table 3). The general quality of results obtained is illustrated in Figures 29 (a,b). A good agreement between experimental and simulated data demonstrates that the simple plug-flow reactor model is *able* to describe the reaction behaviour in the wide rage of the experimental conditions without taking into account heat and mass transfer effects due to high thermal conductivity and developed macroporosity of Ni-Al foam substrates.



Fig. 28. Experimental and simulated (with kinetics – solid lines, thermodynamic predictions –dash lines) data (dry basis) on the effect of the temperature on the methane steam reforming reaction over Ni-Al foam platelet loaded with 5.3% wt.% of 50%LaMnPr+30%NiO+20% YSZ nanocomposite promoted by 0.85%Ru.



Fig. 29. Effect of the operational temperature (a) and linear velocity of the feed gas (STP) (b) on the concentration of components in the product gas. Symbols – experimental data, lines – numerical experiments.

6. Results of catalytic element testing in planar SOFC

The cell tests were performed in the Energy Research Center (Petten, Netherlands) in a test bench with an alumina housing for 5x5 cm² cells (Ouweltjes et al., 2008).

Fuel cells were assembled in configuration Pt grid/LSC/20GCO/8YSZ/Ni-YSZ anode substrate/Ni-Al foam catalytic plate/Ni grid. Here platinum grid was used for cathode current collection, LSC is cathode La-Sr-cobaltite layer, 20GDC- $Ce_{0.8}Gd_{0.2}O_{2-y}$ interlayer between cathode and a thin layer of YSZ supported on a planar Ni-YSZ anode substrate. Nickel mesh as anode current collector was pressed to Ni-Al catalytic plate, so current was passed through it. A stream of CH₄ + H₂O feed (H₂O/CH₄ =2) or hymidified H₂ was passed along the catalytic plate loaded with 5 wt.% of nanocomposite 50% LaMnCrPr + 30%NiO +

20%YSZ promoted by 1.3 wt.% Ru. Air stream was used as oxidant from the cathode side. Electrochemical characterisation was performed by V/I curves and impedance spectroscopy with a Solartron 1255/1287 set-up.

At 600 °C and 700 mV the area specific resistance (ASR) was estimated to be 0.77 Ohm cm^2 without any contribution of catalyst to R_{ohm} , which meets target of operation for intermediate temperature solid oxide fuel cells.

Fig. 30 presents I- V characteristics of this cell with CH₄ or H₂ as a fuel. As follows from these data, at 800 °C cell performance for both types of fuels is comparable, which demonstrates a high efficiency of planar catalytic element in steam reforming of methane. Power density up to 350-850 mW/cm² is achieved in 600-800 °C range, which is promising for the practical application. At CH₄ flow 90 ml/min and 600 °C CH₄ conversion increases from 47 to 55% with increasing current from 0 to 4A. This conversion is rather close to values obtained at this temperature for single platelet with this active component (Fig. 21).



Fig. 30. I- V characteristics of cell equipped with Ni-Al foam-supported nanocomposite catalyst using CH₄ or H₂ as a fuel.

7. Conclusion

Nanocomposite materials developed in this work based upon Ni and doped zirconia electrolyte allow to provide efficient and stable in-cell steam reforming of methane and ethanol required for IT SOFC as well as design of monolithic catalysts of transformation of biofuels into syngas. This is provided by optimization of their composition and preparation procedures ensuring developed interfaces between components activating fuel molecules (Ni, Ni-Pt/Ru alloys) and water molecules (complex oxides with perovskite and fluorite structures). Performance of best compositions supported as porous strongly adhering layers on anode cermets platelets, FeCralloy gauzes and porous Ni-Al foam substrates was estimated as well and demonstrated to be high and stable to meet target of internal reforming of fuels in the intermediate temperature solid oxide fuel cells. No cracking or detachment of layers after reaction was observed. Analysis of methane reforming kinetics catalyzed by structured catalytic elements with supported nanocomposite layers has been carried out. Performance of catalytic plates in IR mode of ECN cell meets target of design of

solid oxide fuel cells with internal reforming of methane by area specific resistance, activity and power density.

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Self-assembled Nanocomposite Oxide Films: Design, Fabrication, and Properties

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1. Introduction

Nanocomposite metal oxides have been extensively investigated in bulk and thin film forms because of their wide range of applications in microelectronics, magneto electronics, and optoelectronics (Ramesh and Spaldin, 2007). Oxide films in nanocomposite form are particularly appealing as the interaction or coupling between the constituents can lead to enhanced or new functionalities (Zheng et al., 2006). Furthermore, the nanocomposite oxide films could lead to their applications as building blocks for the assembly of nanostructures or molecular monolayers (Cheng et al., 2006). A currently primary goal is to fabricate nanocomposite oxide films using a simple and low-cost process. Self-assembly has been the focus of much research in the last four decades. It has proved its ability to offer a rich variety of periodic nanoscale patterns in an easy way (Guiton and Davies, 2007). Recent efforts have striven to bring these two fields together. A major challenge is to control a self-assembled nanocomposite oxide film to create a desired nanostructure (Moshnyaga et al., 2003). In a film-on-substrate geometry, epitaxial composite films can be divided into two forms: horizontal and vertical. These two structures can be reviewed as the building blocks for a desired nanostructure and they are also specific architectures which show lots of potential applications (Yang et al., 2009). This chapter outlines the recent results about the material design, fabrication, and physical properties of these two nanostructures.

2. Material design

An important starting point for our studies was determining which systems have the potential to form clean, heteroepitaxial nanocomposite thin films with ordered nanostructures (MacManus-Driscoll et al., 2008). Since guidelines to the materials selection of nanocomposites have not been presented before, we developed our own as follows: (1) the chosen phases should both have the potential to grow epitaxially on a given substrate; (2) the growth kinetics of the individual phases should be similar so that the two phases can both grow with sufficient crystallinity at a chosen temperature; (3) the two phases of interest should be the most thermodynamically stable when the individual elements are combined; (4) cations with sufficiently different ionic radii are necessary to minimize intermixing of the

phases. It should be pointed out that these are only the necessary conditions for the material design and the sufficient conditions are underway.

3. Horizontal nanostructure

3.1 Overview

An oxide film with horizontal microstructure has also been viewed as a multilayer. Multilayers have been a basically interesting and technologically important research topic in recent years as they exhibit some remarkable and multifunctional properties that do not exist in either of their parents (Ueda et. al, 1998; Ohtomo et. al, 2002). A traditional way to fabricate multilayers is the alternative deposition of various types of thin layers. In the present work, we demonstrate a spontaneous, horizontal, multilayered, and heteroepitaxial oxide film in $(YBa_2Cu_3O_{7-x})_{0.5}$: (BaZrO₃)_{0.5} nanocomposites (Yang et al., 2009). A high critical temperature of 88 K and a surprising field dependent of critical current along the *ab* plane were observed, given that the BaZrO₃ fraction in the films is 50 mol.%, which can be attributed to the self-assembled multilayer structure. The present study represents a new route to prepare multilayers of the oxide materials and holds great promise for other functional systems too.

3.2 Fabrication

Nanocomposite (YBCO)_{0.5}:(BZO)_{0.5} (YBCO:BZO) films were grown on (001) oriented SrTiO₃ (STO) substrates by pulsed laser deposition (PLD) using a XeCl excimer laser (λ =308 nm). A single ceramic pellet with a molar ratio of YBCO/BZO = 1:1 was used as the target. A substrate temperature of 820°C and an oxygen pressure of 200 mTorr were maintained during the deposition. Following the deposition, the films were cooled down to room temperature in an oxygen pressure of 300 Torr without any further thermal treatment. The thickness of films, measured by the cross-sectional transmission electron microscopy (TEM), was 150 nm. The crystal structure was investigated by X-ray diffraction (XRD) using a Siemens D5000 four-circle diffractometer. The critical temperature (T_c) was evaluated by both alternating current (ac) susceptibility and transport measurement techniques. The critical current density (J_c) was obtained by the standard four-point method from a bridge using the 1 μ V/cm criterion, where the films were patterned using standard photolithography with a bridge width of ~250 μ m. The angular and field dependent J_c measurements were conducted in a magnetic field (H) rotated in the plane perpendicular to the plane of the film but always normal to the current $(J \perp H)$, maximum Lorentz force configuration). With the sample immersed in liquid nitrogen the measurement temperature was varied from 65 to 75.5 K.

3.3. Microstructures

Figure 1 shows a typical XRD θ - 2θ scan of the YBCO:BZO films. As can be seen from the figure, the YBCO and BZO phases are well defined and have comparable intensities, as broadly expected for the volume fractions and atomic weights of the compounds. The YBCO shows only (00*l*) diffraction peaks and hence is preferentially oriented along the *c*-axis (perpendicular to the substrate surface). The *c* lattice constant of YBCO, calculated from the (005) peak, is 11.66(96) Å which is close to the bulk value of 11.6805 Å. The BZO shows (001) and (002) peaks, indicating the same *c*-axis orientation. It should be pointed out that besides



Fig. 1. Typical XRD θ -2 θ scan of YBCO:BZO films. A weak BZO (101) peak is denoted by a star. The inset shows phi-scans on STO (101), BZO (101), and YBCO (013) reflections.

the (00*l*) peaks of YBCO and BZO, there is a weak peak at around 2θ =29.4° (shown with a star in Fig. 1) which can be attributed to BZO (101). By comparing the relative intensities of the Bragg peaks associated with the BZO (002) and BZO (101) peaks we estimate that ~97 % of the BZO is *c*-axis oriented. The full-width at half-maximum (FWHM) of the rocking curves for YBCO (005) and BZO (002) are 1.24° and 0.86°, respectively. These values are higher than those for typical pure YBCO and BZO films and the large lattice mismatch between YBCO and BZO is likely responsible for this. The in-plane orientation of the YBCO:BZO films with respect to the major axis of the STO substrate is revealed by phi-scans on the YBCO (013), BZO (101), and STO (101) reflections (shown in the inset of Fig. 1). The orientation relationship is determined to be $(001)_{\rm YBCO} \parallel (001)_{\rm BZO} \parallel (001)_{\rm STO}$ and $[010]_{\rm YBCO} \parallel [010]_{\rm BZO} \parallel [010]_{\rm STO}$, which is in accordance with the pure YBCO and BZO thin films grown on STO substrates.

In order to reveal the detailed microstructure of the YBCO:BZO films, low magnification and high resolution cross-sectional TEM were performed. As can be seen from the low magnification bright-field TEM image (Fig. 2), a multilayer structure is formed throughout the film, i.e., spontaneously ordered alternating layers of YBCO and BZO. The YBCO and BZO layers show thicknesses of 6-10nm and 7-11 nm, respectively. All the layers are continuous in-plane (lateral dimension) up to a micro-meter scale. This is the first time a self-assembled, ordered horizontal nanocomposite film has been observed, although we have observed a self-assembled vertical analogue before in another perovskite system (MacManus-Driscoll et al., 2008; Yang et al., 2009). For YBCO films with BZO, the microstructures previously observed are either random BZO nanoparticles or self-assembled columnar BZO nanorods (MacManus-Driscoll et al., 2004; Kang et al., 2006; Maiorov et al., 2009). The completely different microstructure in the present study originates from an interplay between composition, strain, and growth kinetics (MacManus-Driscoll et al., 2008).



Fig. 2. A low magnification bright field TEM image of a nanocomposite YBCO:BZO film on STO substrate.



Fig. 3. High resolution TEM image with corresponding fast Fourier filtered (FFT) image at the YBCO/BZO interface.

A high resolution TEM (HRTEM) image (Fig. 3) reveals excellent heteroepitaxial growth between the YBCO and BZO layers. The corresponding fast Fourier transformed image from the interface of YBCO and BZO is shown in the inset of Fig. 3. The orientation relations of YBCO/BZO multilayers the are determined to be $(001)_{YBCO} \parallel (001)_{BZO}$ and $[010]_{YBCO} \parallel [010]_{BZO}$, which is consistent with the results from XRD measurements. It is well known that there is a close relationship between the superconductivity and the microstructure in YBCO films (Foltyn et al., 2007). This micron scaled-continuous selfassembled nanolayer structure are believed to contribute to the unique physical properties of YBCO:BZO films.

3.4 Physical properties

It is known that power applications of superconductors require an effective immobilization of vortices, or in other words a high pinning force (Foltyn et al., 2007). The pinning force arises from the presence of localized defects or crystalline imperfections. It has been experimentally shown that nanoscale defects within YBCO materials can pin the magnetic flux lines which translates to a high critical current density (I_c) . Recent efforts have focused on non-superconducting additions to YBCO films to enhance the current carrying capability in applied magnetic fields. For example, Y₂O₃, CeO₂, YBa₂CuO₅, and BZO, because of their good compatibility with YBCO, have been effectively used to increase J_c in YBCO films (Barnes et al., 2004; Haugan et al., 2004). In general, the increase of the BZO content (or the density of pinning sites) initially increases the macroscopic I_{cr} but beyond some optimum density the performance deteriorates. For this purpose, the critical temperature (T_c) and the I_c of YBCO film with different levels of BZO inclusion have been widely investigated. It is a common view that the T_c decreases linearly with increasing BZO concentration (Kang et al., 2007; Peurla et al. 2006). Currently, the reported maximum inclusion of BZO in YBCO films is 8 vol.% (~18 mol.%) where a T_c of 82.8 K was observed. For this concentration, BZO selfassembles in vertical columns along the *c*-axis (Kang et al., 2007). A question that arises is,



Fig. 4. Ac susceptibility of a nanocomposite YBCO:BZO film. The inset shows the resistivity versus temperature characteristic of the same film.

what will happen to the superconductivity of a YBCO film when the BZO inclusion is more than 18 mol.%? It is important to investigate the superconductivity of YBCO:BZO films and the relationship between the physical properties and the unique horizontal nanostructure.

The temperature dependence of ac susceptibility of YBCO:BZO film is shown in Fig. 4. A clear superconducting transition was observed and the on-set T_c was determined to be 88 K which is much higher than the reported value of YBCO films with only 18 mol.% BZO (Kang et al., 2007; Peurla et al., 2006). To confirm the high T_c , the temperature dependence of resistivity measurement was conducted and shown as inset of Fig. 4. A typical linear relationship was found above the transition temperature. The zero resistance temperature of 86 K from the transport measurement agrees well with the result obtained from the ac susceptibility measurement. The resistivity values of the YBCO:BZO film, 600 and 1500 $\mu\Omega$ cm at 100 and 300 K respectively, are one order of magnitude higher than those of a typical pure YBCO film. The layered structure and the highly resistive nature of the BZO lead to the high resistivity of the nanocomposite films. Considering the multilayer structure in the YBCO:BZO films, a T_c of 88 K is not completely unexpected. Huhtinen et al. represented a systematic investigation of superconductivity of YBCO/BZO multilayers fabricated from two different targets by PLD (Huhtinen et al., 2009). T_cs from 88 K to 89.3 K have been observed which dependent on the thickness of BZO layer relative to the YBCO layer and agree well with our results. It should be pointed out that multilayers have been found to increase the density of misfit dislocations at the layer interfaces which compensate the mismatch between YBCO and BZO lattices in the current study (Jia et al., 2002; Pan et al., 2006). This is the main reason that the c lattice constant of YBCO phase is close to the bulk value which also contributes to the high *Tc* value (Huhtinen et al., 2009).

To investigate the flux pinning properties of the YBCO:BZO films, the magnetic field (*H*) dependence of J_c was measured at 65 K and shown in Fig. 5. J_c is normalized to self-field value ($J_c(sf)$ =0.15 MA/cm²) to facilitate the comparison. Firstly, a most striking feature is observed for the case of H//ab, which has an extremely slow J_c field decay. The α value in



Fig. 5. Magnetic field dependence of J_c of a nanocomposite YBCO:BZO film at 65 K. For comparison, a curve for standard pure YBCO films is also included.



Fig. 6. The angular dependence of J_c of a nanocomposite YBCO:BZO film at 65 K and with applied magnetic field of 0.15 and 0.5 T.

the relation of $J_c \sim H^{-\alpha}$ was calculated to be 0.06, which is much lower than the typical value of pure YBCO film (~0.51) and indicates a weaker field dependence of J_c . Secondly, for H//c $J_c(H)$ drops much faster than standard pure YBCO with a α value of 1.48. For the lower concentration doping of BZO in YBCO films, BZO have been reported to self-assemble in vertical columns along the c-axis. And α values from 0.31 to 0.61 have been observed (Kang et al., 2006). By comparing these values with those in the current study, we can see the much lower density of defect along *c* axis and much higher density of defect along *ab* plane in the nanocomposite YBCO:BZO film, which is confirmed by the multilayer structure. It should be pointed out that the $J_c(sf)$ value here is comparable to the reported results of YBCO/BZO multilayers fabricated by two different targets using PLD and could be related to the high resistivity observed.¹⁴ The angular dependence of J_c was also measured and shown as Fig. 6. An enhanced peak for H//ab was observed compared to the typical pure YBCO films and no peak was found for H//c, which are consistent with the multilayer structure and the reported results (Cai et al., 2004).

To summarize, nanocomposite (YBCO)_{0.5}:(BZO)_{0.5} thin films were fabricated by PLD. Both YBCO and BZO phases exhibited spontaneous, horizontal, multilayered, and heteroepitaxial phase assemblage. This unique microstructure led to a T_c of 88 K and a surprising field dependence of J_c along the *ab* plane. The present study represents a new route to prepare horizontal structures of the oxide films and holds great promise for other functional materials too.

4. Vertical nanostructure

4.1 Overview

Nanocomposite films with a vertical architecture such as the nanopillar geometry offer numerous advantages over the conventional horizontal multilayers, such as a larger interfacial area and intrinsic heteroepitaxy in three dimensions (Zheng et. al., 2004; Ramesh et al., 2007). Moshnyaga et al. firstly showed vertical nanopillar films with a composition of

 $(La_{0.7}Ca_{0.3}MnO_3)_{1-x}$: $(MgO)_x$ (Moshnyaga et al., 2003). The structural and magnetotransport properties of the $La_{0.7}Ca_{0.3}MnO_3$ nanoclusters were tuned through the tensile stress originating from the MgO second phase. Zheng et al. reported vertical nanostructures consisting of magnetic spinel CoFe₂O₄ pillars epitaxially embedded into a ferroelectric BaTiO₃ matrix (Zheng et al., 2004). This nanocomposite exhibited strong coupling of the ferroelectric and magnetic order parameters through the three-dimensional heteroepitaxy of the two lattices.

Vertical nanocomposite architectures are not only interesting for achieving multifunctionality, but there is also the potential for enhancing a single functionality through manipulation of the strain of one of the phases by another. Horizontal (lateral) strain within layered heterostructures has been widely studied and indeed is fundamental to many semiconductor device technologies. Recent work has shown that strain control of very thin oxide films can achieve dramatically enhanced functional properties: strain fields perturb ferroelectricity (Nagarajan et al., 2005), and huge changes in the ferroelectric Curie temperature Tc, remanent polarization and structural phase transition temperature have been demonstrated in SrTiO₃ and BaTiO₃ through use of substrate-controlled, coherent inplane biaxial strain (Haeni et al., 2004; Choi et al., 2004). While such lateral strain control experiments are elegant, the thickness over which substantial strains can be maintained is seriously limited, meaning that use of lateral strain control for any potential applications is restricted. Coherently strained films in which the film and substrate in-plane lattice parameters are identical can be maintained only up to a critical thickness (tc), which is on the order of a few nanometres, depending on the amount of the misfit. Above tc, the strain energy becomes so large that it is then energetically favorable to nucleate misfit dislocations (Matthews et al., 1974).

Given this, and that self-assembled vertical nanocomposite systems have enormous potential to control strain vertically in much thicker films with correspondingly large volume, it is surprising that vertical strain control has not been explored previously. In this chapter, $(BiFeO_3)_{0.5}$: $(Sm_2O_3)_{0.5}$ nanocomposite thin films have been fabricated by PLD, where both BiFeO₃ (BFO) and Sm₂O₃ (SmO) phases are spontaneously self-assembled into a vertically ordered nano-columnar structure. The microstructures and vertical interface effects on physical properties are demonstrated.

4.2 Fabrication

Epitaxial nanocomposite (BiFeO₃)_{0.5}:(Sm₂O₃)_{0.5} (BFO:SmO) films were grown on (001) oriented STO and Nb-doped SrTiO₃ (Nb-STO) substrates by PLD using a XeCl excimer laser (λ =308 nm). A single ceramic pellet with a molar ratio of 0.5(BiFeO₃)-0.5(Sm₂O₃) was used as the target. BFO:SmO were grown at 670°C with a XeCl excimer laser operated at 5 Hz laser repetition rate, and at 100 mtorr oxygen pressure. The thickness of films, measured by cross-sectional TEM, was 150 nm. For comparison, pure BFO and SmO thin films with the same thickness were also deposited on (001) oriented STO and Nb-STO substrates using the same processing parameters. It should be noted that the single-crystal conductive Nb-STO substrate not only provides a good template for epitaxial growth of BFO, SmO, and BFO:SmO films, but also functions as a bottom electrode for the electrical measurements. The crystal structures of thin films were investigated by high-resolution XRD (HRXRD) and TEM. Nuclear resonance backscattering spectrometry with a He⁺ beam energy of 3.045 MeV was used to measure oxygen concentration in the pure BFO film. Compared with traditional Rutherford backscattering spectrometry, the strong and narrow resonance

provides a better sensitivity and depth resolution for oxygen detection. In our measurement, the beam energy was chosen in a way that resonant scattering occurs in the film not in the substrate. For electrical property measurements, vertical sandwich capacitors with a configuration of Pt/BFO:SmO/Nb-STO (or Pt/BFO/Nb-STO, Pt/SmO/Nb-STO) were fabricated, where the Pt top electrodes with an area of 1×10^{-4} cm², defined by a lift-off lithography process, were deposited by sputtering. The frequency dependent capacitance (*C-f*) and dielectric loss ($tan \delta$ -f) were measured using a HP4194A impedance analyzer. The current-voltage (*I-V*) characteristics of the capacitors were measured using a Keithley 487 picoampere meter with a delay time of 5 seconds.

4.3 Microstructures

In order to reveal the microstructure of self-assembled BFO:SmO nanocomposites, planview and cross-sectional transmission electron microscopy was performed. As can be seen from the plan-view TEM image (Fig. 7a), a checker-board structure is formed. In other words, an ordered alternative growth of BFO and SmO domains (marked as B and S, respectively) is self-assembled. Each of the domains has a lateral dimension of ~15 nm. A low magnification bright-field cross-sectional TEM image (Fig. 7b) also shows that the BFO and SmO domains have grown alternately and vertically aligned with an average column size of 15 nm. A high resolution TEM (HRTEM) image (Fig. 7c) reveals excellent heteroepitaxial growth of the BFO and SmO nanocolumns on the STO substrate. It is interesting to note that there is a lattice matching relation along the vertical boundaries between the BFO and SmO. The matching spacing is about 1.3 nm. The corresponding fast Fourier transformed images from the areas of the BFO, SmO and STO are shown as an insert of Fig. 7c. The orientation relations of the BFO:SmO nanocomposite and the substrate are determined to be $(002)_{BFO}//(004)_{SmO}//(002)_{STO}$ and $[200]_{BFO}//[440]_{SmO}//[200]_{STO}$, which is in accordance with the pure BFO and SmO thin films grown on STO substrates. The BFO:SmO nanocomposite thin film provides the opportunity to investigate the vertical interface effect on the physical properties of the individual BFO and SmO phases by comparison to the pure-phase films.

4.4 Physical properties

For epitaxial metal oxide films, interfaces always play a critical role in controlling the structural and electrical properties. Both experimental and theoretical works have demonstrated the impact of lateral interface on the physical properties of either single-phase thin films or superlattices (Junquera et al., 2003; Ohtomo et al., 2004; Choi et al., 2004; Reyren, et al., 2007). For instance, Reyren *et al.* reported superconductivity in the electron gas formed at the interface between LaAlO₃ and SrTiO₃ (Reyren et al., 2007). There have also been reports on the lateral interface effect on the physical properties of ferroelectric thin films, such as size effects, critical thickness, and strain and coupling enhanced ferroelectricity (Lee et al., 2005; Jia et al., 2007). Compared with the lateral interface, the effect of vertical interface on the physical properties of metal oxide films is profound. However, there are only a few reports because of the lack of vertical nanocomposites with ordered structures on a large scale (Ramesh et al., 2007). Here we demonstrate the vertical interface effect on lattice parameters, dielectric properties, and leakage current of BFO:SmO nanocomposite films. To illustrate the improved functionalities of our nanocomposites, we compare to the physical properties of pure BFO and SmO thin films.



Fig. 7. TEM images of the BFO:SmO nanocomposite film on an STO substrate: (a) Plan-view showing an ordered checker-board structure (B represents BFO, S represents SmO); (b) low magnification cross-sectional view showing the alternating columns of BFO and SmO; (c) high resolution cross-sectional view with corresponding fast Fourier filtered (FFT) images from BFO, SmO and STO areas.

BFO:SmC nanocomposite		D:SmO posite film	pure BFO	pure SmO	Bulk	Bulk
	BFO	SmO		thin film	DFU	5110
out-of-plane						
lattice constant (Å)	3.905	11.088	3.981	10.886	3.962	10.920

Table 1. Out-of-plane lattice constants of individual BFO and SmO phases in the BFO:SmO nanocomposite film, and pure BFO and SmO thin films on STO or Nb-STO substrates. The thicknesses of all the films are 150 nm. Bulk values are also shown.

Table 1 shows the out-of-plane lattice constants of individual BFO and SmO phases in the BFO:SmO nanocomposite. In comparison, lattice parameters of pure BFO and SmO thin films and bulk values of BFO and SmO are also included in the table. The out-of-plane lattice constant of the BFO phase in the nanocomposite is 3.905 Å, compared with a value of 3.981 Å and 3.962 Å for the pure BFO film and the bulk BFO respectively. It should be noted that the BFO phase in the nanocomposite is under compressive strain (-1.46%) in contrast with a tensile strain (+0.47%) for the pure BFO film. On the other hand, the vertical strain state of SmO phase in the nanocomposite is switched from compression (-0.31%) to tension (+1.54%), opposite to the strain switching in the BFO phase. It is apparent that the dominant strain mechanism for the BFO and SmO phases arises from the vertical interface, rather than from the lateral interface. As the absolute values of the vertical strain in the nanocomposite are 3-5 times of those in the pure films, the vertical interface is more efficient to control the out-of-plane lattice constant than the lateral interface.

To understand the vertical interface effect on the electrical properties of the nanocomposite, we measured the dielectric properties of BFO:SmO, BFO, and SmO thin films. As can be seen from the TEM images, the BFO and SmO columns of the nanocomposite are connected in parallel if one considers a vertical capacitor structure of Pt/BFO:SmO/Nb-STO. Sherman *et al.* have studied the dielectric properties of the columnar composite by using an equivalent electrical circuit consisting of two capacitors connected in parallel (Sherman et al., 2006; Yamada et al., 2006). In the case of our (BFO)_{0.5}:(SmO)_{0.5} nanocomposite films, if we assume the equal surface area of two different phases (see the TEM image), the dielectric constant and dielectric loss can be expressed as:

$$\varepsilon_{BFO:SmO} = \frac{1}{2} (\varepsilon_{BFO} + \varepsilon_{SmO}) \tag{1}$$

$$\tan \delta_{BFO:SmO} = \frac{\varepsilon_{BFO} \tan \delta_{BFO} + \varepsilon_{SmO} \tan \delta_{SmO}}{\varepsilon_{BFO} + \varepsilon_{SmO}} , \qquad (2)$$

where, the $\varepsilon_{BFO:SmO}$, ε_{BFO} , and ε_{SmO} are the dielectric constants of the BFO:SmO nanocomposite film, the pure BFO film, and the pure SmO film. The tan $\delta_{BFO:SmO}$, tan δ_{BFO} , and tan δ_{SmO} are the dielectric losses of the BFO:SmO nanocomposite film, the pure BFO film, and the pure SmO film. Because there is no observable intermixing of two individual phases from the HRTEM image, we ignore any reactive products between the BFO and the SmO in nanocomposite film. It is noted that there is the possibility of some Sm³⁺ substitution for Bi³⁺ in the BFO nanocolumns, but this isovalent substitution should not alter the dielectric or leakage properties of the film since no charge compensating defects would be

required to form. Fig. 8a shows the measured dielectric constants of BFO:SmO, BFO, and SmO thin films as a function of frequency. The calculated dielectric constant of the nanocomposite from Eq. (1) is 92. The difference between the experimental and calculated dielectric constants of BFO:SmO nanocomposite film is about 4%.



Fig. 8. Dielectric constants (a) and dielectric losses (b) of BFO:SmO, BFO, and SmO thin films as a function of frequency.

Thus, the dielectric constant of such a BFO:SmO nanocomposite can be well described by an equivalent parallel circuit model. In other words, considering that the dielectric constant of the nanocomposite should be controlled by the higher dielectric constant phase, the strong vertical strain of BFO phase shows little influence on the dielectric constant of the nanocomposite. This is possible considering that BFO has a high Curie temperature (~1103 K) (Michel et al., 1969). For ferroelectric materials at a temperature (300 K in this case) that is far away from the Curie temperature, the strain shows little influence on the dielectric properties directly.

Fig. 8b shows the dielectric losses of BFO:SmO, BFO, and SmO thin films as a function of frequency. The calculated dielectric loss of BFO:SmO nanocomposite from Eq. (2) is 0.050, which is much larger than the experimental value of 0.015. It is interesting to consider the source of the large reduction in the dielectric loss of the BFO:SmO nanocomposite. As can be seen from Eq. (2), the reduction of the dielectric loss must originate from the BFO phase, since the dielectric properties of the BFO phase should control the overall dielectric properties of the nanocomposite. It has been widely reported that there is a close relationship between leakage current and dielectric loss in ferroelectric materials. Ferroelectric materials with lower leakage current typically exhibited smaller dielectric loss (Joshi, et al., 2000). For example, Wang *et al.* reported that reduction of oxygen vacancies in doped BFO films reduced the leakage current and then the dielectric loss (Wang et al., 2006). Figure 9 shows the leakage current density *vs.* electric field (*J-E*) characteristics of BFO:SmO, BFO, and SmO thin films. Because the leakage current density of the SmO thin film at low electric fields reaches the limit of our measurement, we only show the leakage current


Fig. 9. Leakage current density *vs*. electric field (*J*-*E*) characteristics of BFO:SmO, BFO, and SmO thin films. The dotted line shows the measurement limit.

density at an electric field of ±250 kV/cm. As illustrated in Fig. 9, the resistivity (ρ) of different films at a given electric field follows the relationship: $\rho_{SmO} >> \rho_{BFO:SmO} >> \rho_{BFO}$. If we consider BFO and SmO columns in the BFO:SmO nanocomposite as resistors connected in parallel with a device configuration of Pt/BFO:SmO/Nb-STO, the leakage current will be controlled by the BFO because of the much higher resistance of SmO. In other words, the leakage current of the BFO phase within the nanocomposite will be roughly the same as the total leakage current of the entire BFO:SmO nanocomposite film. This implies that the leakage current density of the BFO phase in the nanocomposite film is much lower than that of a pure BFO film. This may explain the much lower experimentally observed dielectric loss of the nanocomposite film relative to the loss calculated from Eq. (2).

It is important to investigate the origin of the reduction of the leakage current density of the BFO phase in the nanocomposite film. It has been widely reported that oxygen vacancies (V_{OS}), rather than Fe²⁺ ions, are the main cause of high leakage current densities in BFO thin films. Efforts have been made to reduce the V_{OS} by introducing post-annealing in an oxygen atmosphere, doping with higher valence ions, and oxygen ion implanting (Wang, et al., 2006). To investigate the oxygen vacancies effect on the leakage current density in the present study, some pure BFO films and BFO:SmO nanocomposites were subjected to an in situ annealing in oxygen (~500 Torr) at a temperature of 390°C for 60 mins. Nuclear resonance backscattering spectrometry (NRBS) was used to measure the oxygen concentration in the as-deposited and annealed BFO films (as shown in Fig. 10). In principle, NRBS is identical to the well known Rutherford backscattering spectrometry, with an exception that higher projectile beam energy is used in NRBS. Higher energy allows the interaction between the projectile and the target nucleus to overcome the Coulomb repulsive force barrier due to a very close encounter between incident particle and the target nucleus. As a result, the scattering cross section becomes non-Rutherford and often exhibits a narrow



Fig. 10. Oxygen resonance peaks of as-deposited and annealed BFO films.

and strong resonance peaks that sometimes can be orders of magnitude stronger than the Rutherford value. Multiple light elements such as B, C, N, and O can be measured with NRBS simultaneously. In our measurement, the beam energy was chosen in a way that resonant scattering occurs in the film (not in the substrate). Compared with traditional Rutherford backscattering spectrometry using 2 MeV He⁺ beam, the strong and narrow resonance at 3.045 MeV provides a better sensitivity (~10 times better) for oxygen detection. Oxygen concentration was determined by fitting oxygen peak in the measured spectrum using SIMNRA, popularly used data reduction software in ion beam analysis. Resonance scattering cross sections in the SIMNRA database was cross-checked using a known oxygen standard such as a bare STO substrate. The oxygen concentration is determined to be 5.14×10^{17} and 5.44×10^{17} at./cm² for as-deposited and annealed BFO films, respectively. The ideal oxygen concentration for stoichiometric BFO film is estimated to be 5.79×1017 at./cm². The NRBS results clearly show that there are V_{OS} in BFO films: 11.2% deficient in the asdeposited film and 6.0% deficient in post-annealed film compared to the ideal case. At the same time, the V_{OS} can be effectively reduced by the post-annealing which is consistent with reported results (Wang et al., 2006). Furthermore, the leakage current densities of asdeposited and annealed BFO and BFO:SmO films were measured and shown as Fig. 11. It is obviously that the leakage current density of annealed BFO film is 2 orders of magnitude lower than that of the as-deposited BFO film. Therefore, the reduced oxygen vacancies contributed to the lower leakage current density in the annealed BFO films.

As we discussed earlier, the leakage current density of the BFO:SmO nanocomposite is much lower than that of the BFO films. Considering the nature that the leakage current in nanocomposites is controlled by the BFO phase and the relationship between the oxygen vacancies and the leakage current in BFO films, the much lower leakage current density in nanocomposite implies the reduced oxygen vacancies in the BFO phase. In the other side, it is worth noting that in Fig. 11 two curves for as-deposited and annealed BFO:SmO nanocomposites are almost overlapped, especially in the higher electric fields. This further



Fig. 11. Comparison of leakage current densities of as-deposited and annealed BFO and BFO:SmO films.

confirmed that the oxygen vacancies in the BFO phase were reduced and then the postannealing shows little influence on them. Considering the microstructure of the BFO:SmO nanocomposites, one explanation for the reduced oxygen vacancies in BFO phase is that there is oxygen transportation from the SmO to the BFO. Theoretically, the possibility of oxygen transportation is proportional to the interface area. The vertical interfacial area of each BFO column is 2*at* in a nanocomposite system, where *a* is the average dimension of the column and *t* is the film thickness (MacManus-Driscoll et al., 2008). On the other hand, the lateral interfacial area for a pure BFO film on a Nb-STO substrate (assuming the same dimension) is simply $a \times a$. It is obvious that the interfacial area of BFO phase in the nanocomposite can be much higher (considering a~15 nm and t~150 nm). Then, the possibility of oxygen transportation from the SmO to the BFO in the nanocomposite is much larger than that from substrate to pure BFO film. In other words, the larger vertical interfacial area in BFO:SmO nanocomposites contribute to the reduction of leakage current density of the BFO phase, and so the reduced dielectric loss.

To further understand the dielectric and leakage properties, we investigated the leakage mechanism of nanocomposit BFO:SmO films. Figure 12 shows $\log(J)$ vs $\log(E)$ characteristics of as-deposited BFO, annealed BFO, and nanocomposite BFO:SmO films at positive bias. The slopes are close to 1 and the leakage currents show Ohmic behaviour at relatively lower electric fields. In the high electric field range (>~75 kV/cm), the $\log(J)$ -log(*E*) plots are linear and the slopes are close to 2, which agree well with the SCLC mechanism. The SCLC is considered as a normal leakage behaviour and correlates with oxygen vacancies in BFO materials (Wang, et al., 2006). In addition, we also studied the *J*-*E* characteristics of as-deposited BFO, annealed BFO, and BFO:SmO films at negative bias. In the low electric field range (<50 kV/cm), the log(*J*) vs log(*E*) plots are linear and the slopes are around 2 (not shown), indicating the conduction is controlled by SCLC. Figure 13 shows (a) $\ln(J/E^2)$ vs (1/E) characteristic of as-deposited BFO film and (b) $\ln(J/E)$ vs $E^{1/2}$ characteristics of



Fig. 12. Log(J) vs log(E) characteristics of as-deposited BFO, annealed BFO, and BFO:SmO thin films at positive bias.



Fig. 13. (a) $Ln(J/E^2)$ vs (1/E) characteristic of as-deposited BFO film; (b) ln(J/E) vs $E^{1/2}$ characteristics of BFO:SmO and annealed BFO films at negative bias. The calculated optical dielectric constants are shown.

BFO:SmO and annealed BFO films at negative bias. For the as-deposited BFO film, the leakage currents show F-N tunneling behaviour in the electric field above 180 kV/cm. On the other hand, the $\ln(J/E)-E^{1/2}$ plots of BFO:SmO and annealed BFO films show linear relation in the electric field above 50 kV/cm. The ε_{opt} of BFO:SmO and annealed BFO films, with values of 6.45 and 5.19 respectively, can be calculated from the slopes of $\ln(J/E)$ vs $E^{1/2}$ plots. The optical refractive index (*n*) can be determined from the optical dielectric constant

with a relationship of $n = \sqrt{\varepsilon_{opt}}$. For BFO:SmO and annealed BFO films, the *n* can be evaluated as 2.54 and 2.28 respectively. The *n* can also be measured directly from the spectroscopic ellipsometry (SE) measurement through model based analysis. The measured *n* values are 2.42 and 2.58 at the wavelength of 633 nm for BFO:SmO and annealed BFO films, respectively. The *n* values calculated from slopes of $\ln(J/E)$ vs $E^{1/2}$ plots are in good agreement with the SE extracted results, strongly suggesting P-F emission behavior in the electric field range above 50 kV/cm. The P-F emission is commonly considered as acceptable leakage behaviour and the likely trap centre is Fe²⁺ in BFO films. Therefore, the leakage mechanisms of BFO:SmO nanocomposite films are the same as those of annealed BFO films. This is in consistent with the reduced V_{OS} in BFO phase in the nanocomposite films.

To summarize, self-assembled BFO:SmO nanocomposite films have been deposited with three-dimentional heteroepitaxy having an ordered nano-columnar structure on a large scale. The vertical strain is the dominant factor determining the out-of-plane lattice parameters and strain state of the BFO and SmO phases. The dielectric constant of the nanocomposite is not a function of strong vertical strain and can be modeled very well by an equivalent parallel circuit. The nanocomposite shows a lower than expected dielectric loss, due to the presence of a larger vertical interfacial area in the nanocomposite, causing a reduction of the oxygen depletion in the BFO phase relative to a pure BFO film. The present work represents a new way to enhance functionalities of oxide films by both strain coupling and increase of interfacial area in the vertical nanocomposite architecture.

5. Conclusions and future research

In conclusion, by detailed material design and fabrication, self-assembled nanocomposite oxide films with horizontal and vertical architectures have been achieved on YBCO:BZO and BFO:SmO systems respectively. The microstructures, physical properties, and relationships between them have been investigated. It has been found that the interfacial and strain engineering play a critical role to determine the nanostructure and then the unique functionalities. Future work will focus on the mechanism of self-assembly, the full conditions of material design, and the way to control the microstructures and functionalities. The self-assembled nanocomposite films with ordered nanostructure hold great promise for novel applications on microelectronics, optoelectronics, photonics, and energy storage (MacManus-Driscoll et al., 2008; Yang et al., 2009). The work in this chapter also opens up a new avenue to control a self-assembled system to create a desired nanostructure.

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