Introduction to Polymer Compounding: Raw Materials, Volume 1

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http://www.polymer-books.com

First Published in 2014 by

Smithers Rapra Technology Ltd
Shawbury, Shrewsbury, Shropshire, SY4 4NR, UK

A catalogue record for this book is available from the British Library.

ISBN: 978-1-90903-060-2 (hardback)
978-1-90903-062-6 (ebook)

Typeset by Integra Software Services Pvt. Ltd.

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Preface

Remaining competitive will increasingly depend upon continuing the rapid adaptation and incorporation of technical advances into processing. Technological steps to reduce the cost of end products will often be associated with such advancement. *Introduction to Polymer Compounding: Raw Materials, Volume 1* describes the essential factors to be considered to reduce costs as well as waste from processes. The aim of the book is to emphasise how knowledge about compounding will support the sustainable production of polymeric compounded materials that are safe for the environment.

This book helps to choose a path on the basis of an idea, fully described in the chapters, about how one can use the compounding requirements for polymer processing with a much greater understanding and broader approach, as well as providing an overview of compounding ingredients.

The book will be useful in understanding the raw materials and their potential application in industry and academia. By suggesting a possible classification of additives, and discussing compounding, the chapters attempt to illuminate the similarities in research and processing disciplines. The book helps to achieve the goals of increased efficiency, productivity and profitability, as well as discussing the benefits that can be provided by compounding, with a view to achieving environmental and economic sustainability in polymer processing.

I give thanks to God, who has given me the great opportunity to produce such a book, with the benefit of my long experience of 27 years in the plastics processing field. I thank Helene Chavaroche and Eleanor Garmson of Smithers Rapra Information Ltd, my gurus and professors, and finally my family members, who helped me during the course of producing the book. Finally, I thank Himachala Ganga and Masters Venkatasubrmanian and Sailesh for their help with typing.

Dr. Muralisrinivasan N S

Madurai

September 2014

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Introduction

The majority of polymers are petrochemical-based and have been increasingly used in large quantities because of their low cost, light mass, favourable functionality and good barrier properties, as well as their versatility in terms of mass production. It is well known that commercial polymer processing operations, including injection moulding, extrusion, blow moulding and various coating methods, require the compounding of polymeric materials. Without compounding, polymers exhibit flow instabilities, which manifest themselves as distortions on the product surface. These distortions pose a limitation to the production rate that threatens the economic feasibility of such processes [1–4]. Compounding is therefore an important part of polymer processing.

Compounding helps to produce new polymer products with specific properties relevant to their intended subsequent use, either by blending different polymers together or by adding additives, fillers or reinforcing agents. The main aim is to produce polymer blends or modified plastics to reduce raw material costs and to improve product properties without having to fall back on using expensive polymers [5]. The most important advantages of polymers result from compounding processes, for example via the mixing of additives and fillers with the polymers, thereby enabling the required end product performance and properties to be achieved.

Compounding involves using a large range of additives and fillers to regulate the behaviour of polymers when in use. Accordingly, it is a multidisciplinary science involving the selection and blending of appropriate combinations of polymer and other ingredients to meet the performance, manufacturing, environmental and cost requirements for the end products and their commercial use. This involves chemistry, physics, mathematics and polymer science, and, in many cases, classical scientific methods can be used to analyse the interactions involved to predict the properties that will be achieved in the compounded polymer. Environmental concerns also encourage polymer compounding, by utilising available polymers to create new polymers via blending or by enhancing properties through the addition of appropriate additives. Compounding combines the influences of the polymer, additives and fillers on the rheology of the melts, together with mechanisms involved during the melt mixing process. The physical and chemical nature of the polymer and other components will therefore determine the functional role of the compounding.

In summary:

- Polymers exhibit flow instabilities.
- Flow distortions pose a limitation on the production rate.
- Compounding is used to produce polymer blends or modified plastics.
- The physical and chemical natures of the polymer and other components are involved in compounding.
- Environmental concerns promote polymer compounding.
- Compounding involves chemistry, physics, mathematics and polymer science, and in many cases classical scientific methods.

References

1. C.J.S. Petrie and M.M. Denn, *AIChE Journal*, 1976, **22**, 209.
2. A.V. Ramamurthy, *Journal of Rheology*, 1986, **30**, 337.

3. D.S. Kalika and M.M. Denn, *Journal of Rheology*, 1987, **31**, 815.
4. R.G. Larson, *Rheologica Acta*, 1992, **31**, 213.
5. R. Gächter and H. Müller in *Kunststoff-Additive*, Hanser Verlag, Munich, Vienna, New York, NY, USA, 1989.

2 Polymer Materials

Polymers are macromolecules that differ from other substances in a number of ways:

- By the size of the molecules;
- By consisting of thousands or tens of thousands of atoms; and
- By being a more complicated system than low molecular weight (MW) solids or liquids.

The atoms of a polymer are held together firmly by valence bonds, forming a single entity. In polymer substances, weaker van der Waals forces have an effect on the components of the macromolecules that form the system. Polymer behaviour is viscoelastic, which is closely connected with slow relaxation processes in systems.

In comparison with other materials, polymers have many advantages, including stiffness and strength. They have a well-balanced supply, are low in cost and their processing technology is improving. Indeed, the majority of products around the world are made from polymers. They are used in everything from cheap daily necessities to expensive industrial applications. They can be recycled or modified to provide new polymeric products via compounding with other polymeric materials as blends, alloys and so on [1].

2.1 Classification

Polymers are classified, based on the recycling or reprocessing of the material, as:

- Thermoplastic polymeric materials, or
- Thermoset polymeric materials.

Material data are helpful before troubleshooting processing problems. Furthermore, the successful operation of facilities for the polymer processing of materials with different ingredients demands close control of processing parameters during compounding. Indeed, the properties and therefore the performances of polymeric materials achieved *via* compounding are of industrial importance.

2.1.1 Thermoplastics Polymeric Materials

Thermoplastics polymeric materials have traditionally been the workhorse of industry because of their ease of processing. The application of heat and pressure to provide sufficient softening imparts appropriate flow to thermoplastic materials. No chemical reaction takes place during this heating. The material remains in the plastic state as long as the temperature is maintained. In moulding operations, thermoplastic materials are heated to the softening point, pressure is applied, the mould is cooled, and the product is removed. Reprocessing of such materials is possible.

2.1.2 Polyethylene

Polyethylene (PE) is the second largest of the commodity polymers. It is one of the most extensively used polymers because of its widespread practical applications, including medical devices, food packaging, automobiles and many others [2–5]. It is difficult to modify PE to achieve weather and fire resistance without losing its impact strength.

It has a high mould shrinkage factor, and is prone to warpage, low stiffness and temperature resistance with no transparency. It has a tensile strength and ultimate mechanical properties that are important to its use in engineering applications such as water and gas pipes. The properties of PE are tabulated in **Table 2.1**.

MW, MW distribution and side-chain branches in PE influence its material properties, including melting point and crystallinity. Linear low-density PE is more easily processed than high-density PE due to the presence of side-chain branches. The combination of stiffness and stress-crack resistance of the material are improved by the presence of these side chains [6, 7]. To improve processing, polymers with different MW can be melt-blended, but with the resultant problems and cost.

Table 2.1 Properties of PE

Parameter	**Unit**	**Value**	**Reference**
Density	g/cc	0.941–0.965	[8]
Coefficient of linear expansion	at 20°C, 10^{-6} K^{-1}	(14–20) × 10^{-5}	
Deforming temperature range	°C	180–220	
T_m range	°C	125–140	
Vicat softening point	°C	134	[9]
Crystallinity	%	56–58	[10]
T_m	°C	103–133	
T_m: Melting temperature			

2.1.3 Polypropylene

Polypropylene (PP) is semi-crystalline polymer used in many industrial applications, including extruded pipes, films and fibres, and injection-moulded and thermoformed parts, as a result of its physical, thermal and chemical properties (low density, high melting point, stiffness, good impact properties, chemical inertness, good clarity, excellent barrier properties and low cost). PP is used for its low density, stiffness, transparency and temperature resistance when impact strength is not a consideration. The properties of PP are listed in **Table 2.2**.

Table 2.2 Properties of PP

Parameter	**Unit**	**Value**	**Reference**
Density	g cm^{-3}	0.906	[8]
Heat distortion temperature	°C	85–115	
Coefficient of linear expansion	–	$(11–18) \times 10^{-5}$	
T_m	°C	165–176	[11, 12]
Melt flow index	g/10 min	10	[12]

2.1.4 Polystyrene

Polystyrene (PS) is a commodity plastic manufactured on a large scale. It is considered to be nonpolar. The applications of PS are limited in high-performance engineering products due to its brittleness. It is used as light coverings or in the transparent parts of electrical appliances. To overcome brittleness, PS has been extensively modified, and its copolymers and blends represent the most versatile class of polymeric materials [13]. Its properties are listed in **Table 2.3**.

PS is very resistant to biodegradation. Microbial degradation of PS proceeds at a slow rate. Photodegradation can increase the rate of biodegradation of PS, but it still remains very low and is rather difficult to determine. Polymer blends obtained by mixing PS with biodegradable components such as cellulose or starch demonstrate an increase in biodegradation rate [14–16].

Table 2.3 Properties of PS

Parameter	Unit	Value	References
Density	g/cc	1.04–1.11	[8]
Heat distortion temperature	°C	70–100	
Coefficient of linear expansion	–	$(6–21) \times 10^{-5}$	
Dipole moment	D	0.26	[17]
T_m	°C	275	[18]
Melt flow rate	g/10 min	1.6	[19]
T_g	°C (amorphous)	100	[20]
	°C (crystalline)	110	[21]

T_g: Glass transition temperature

2.1.5 Polyvinyl Chloride

Polyvinyl chloride (PVC) is the second largest volume material. It is a semi-crystalline polymer. Its melting during processing has a great influence on the properties of the end product. As a major class of common plastics, it has many unique mechanical properties, and is suitable for a wide range of applications. It obtains the best results as a consequence of its overall material characteristics, including mechanical properties, processability and thermal stability.

It is easily compounded as a rigid material and is known for its soft, supple feel. PVC is a material of relatively low cost with high specific gravity. It has good chemical resistance, is non-burning and exhibits good weather resistance. There is a possibility of producing a transparent product and it can bond with solvents. It can be pigmented easily to produce bright colours with good long-lasting colour stability. Its disadvantages are its relatively low tensile and flexural strength and a heat deflection temperature that limits its use in hot and load-bearing applications. The properties of PVC are listed in **Table 2.4**.

PVC is one of the most heavily consumed synthetic polymers because of its easy availability, low cost and the feasibility of moulding it into various foams. PVC is used in biomedical applications, such as in the fabrication of disposable devices like storage containers for biological fluids (e.g., blood), catheters and so on [22, 23].

One of the important properties of PVC resin is its ability to rapidly absorb plasticisers and other compounding ingredients. This ability is closely related to the morphology of the resin particles. The unusual morphology of PVC originates from the fact that PVC is insoluble in the monomer (vinyl chloride) and precipitates as particles about 1 µm in diameter, as reported by Bort and co-workers [24].

Table 2.4 Properties of PVC

Parameter	Unit	Value	References
Density	g/cc	1.35–1.40	[8]
Heat distortion temperature	°C	70–90	
Coefficient of linear expansion	at 20°C 10^{-6} K^{-1}	$(6–8) \times 10^{-5}$	
Crystallinity	%	5–10	[25]
Thermal conductivity	10^{-4} cal/s-cm^2 °C	3.5–5.0	[26]
T_g	°C	75–105	[11]

2.1.6 Biodegradable Polymers

Biodegradable polymers are one of the most interesting areas of material science, in which chemical, medical and environmental scientists are contributing to human health care, improving quality of life, protecting the environment from white pollution, and reducing dependence on fossil fuels. A great number of polymers have been developed as potential biodegradable materials due to their various compositions, special structures and excellent properties, which cover a wide range of applications [27–29].

As a result of their excellent biocompatibility, polylactones such as polylactic acid (PLA) and poly(ε-caprolactone) (PCL), and their copolymers, are becoming the most commonly used synthetic biodegradable polymers in the medical field, with their inherent and important renewable feature – biodegradability – and other important properties such as transparency, excellent film-forming properties *via* casting for coatings, and good thermal, permselective, mechanical and processing properties [28].

2.1.6.1 Poly(ε-caprolactone)

PCL is crystalline in nature. It has flexibility and toughness [30]. The normal form of PCL is crystalline and substantially fully hydrogen-bonded. The structure of PCL is illustrated in **Figure 2.1**. **Table 2.5** illustrates the properties of PCL.

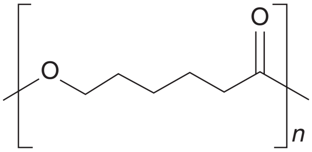


Figure 2.1 Structure of PCL

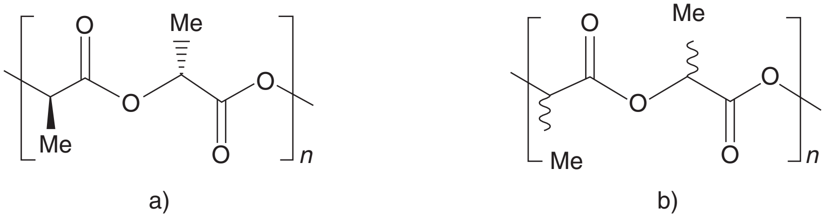
Table 2.5 Properties of PCL

Parameter	Unit	Value	References
Intrinsic viscosity, η	dl g^{-1}	1.26	[31]
Density	g cm^{-3}	1.131	
T_m	°C by DSC	222.8	
	°C	63	[30]
T_g	°C	-65	

2.1.6.2 Polylactic Acid

PLA is a biodegradable polymer used in tissue engineering for medical applications. Based on optical rotation, PLA materials include the dextrorotatory (D) and dextro, levo rotatory (D,L) forms. The properties of PLA are given in **Table 2.6**. The structures of the different forms are identical, but they differ in their crystallinity. PLA (D) has a crystalline structure and is tough, with melting temperature T_m = 180 °C and glass transition temperature T_g = 67 °C, whereas PLA (D,L) has an amorphous structure (with toughness) and T_g = 57 °C [30].

PLA (D) and (poly(D,L-lactic acid) (PDLLA)) (D,L) (**Figure 2.2**) are biodegradable polymers used in tissue engineering for medical applications. They are chemically identical but differ in their crystallinity. PLA (D) is crystalline and tough and PDLLA (D,L) is amorphous [32].



a)

b)

Figure 2.2 Structure of isomers of PLA: (a) poly(D-lactic acid) and (b) poly(D,L-lactic acid)

Table 2.6 Properties of PLA

Parameter	Unit	Value	References
Intrinsic viscosity, η	dl g^{-1} (linear molecule)	2.41	[33]
Crystallinity	%	37	[34]
T_m	°C	60	[35]
	°C (homo polymer)	175	
T_g	°C	-60	
	°C (homo polymer)	60	

2.2 Engineering Polymers

Engineering polymers are characterised by high ratings for mechanical, thermal, electrical and chemical properties. Their properties are reproducible and predictable and also retained over a wide range of environmental conditions. Distinct from the high volume/low volume commodity plastics, engineering polymers are in a special category [36].

2.2.1 Acrylonitrile-butadiene-styrene

Acrylonitrile-butadiene-styrenes (ABS) are graft copolymers widely used in many applications. ABS polymers are based on three monomers: acrylonitrile, butadiene and styrene. Because of its good balance of properties, its toughness/strength/temperature resistance coupled with its ease of moulding and high-quality surface finish, ABS has a very wide range of applications. It is widely used as an engineering thermoplastic, and also demonstrates good mechanical behaviour and chemical resistance.

ABS consists of a styrene/acrylonitrile continuous phase partially grafted to a dispersed butadiene phase. Butadiene acts as an impact modifier, and imparts excellent mechanical properties to the material. Improvement of the impact-modifying properties of ABS during melt processing and product use focuses on protecting the polybutadiene phase from degradation. Polybutadiene is particularly susceptible to oxidation due to the presence of residual double bonds [37]. The properties of ABS are tabulated in **Table 2.7**.

After periods of exposure to heat and oxygen, the mechanical properties of ABS, including impact strength and elongation to break, deteriorate as a consequence of this polymer degradation, inducing premature failure [38].

Table 2.7 Properties of ABS

Parameter	Unit	Value	References
Density	g/cc	1.07	[8]
Heat distortion temperature	°C	110–121	
Coefficient of linear thermal expansion	at 20°C $10^{-6}\,K^{-1}$	(6–21) × 10^{-5}	
T_g	°C	88–120	[11]
T_g rubber phase	°C (from styrene butadiene rubber)	-55	[39]
	°C (from nitrile rubber)	-40	
Surface resistivity	Ω/sq	~10^{15}–10^{16}	[40]

2.2.2 Polymethyl Methacrylate

Polymethyl methacrylate (PMMA) is a typical transparent amorphous polymer. It has been widely used as an important material in optical devices. It has several advantages, including good flexibility, high strength and excellent dimensional stability; however, it suffers from shortcomings such as poor heat resistance, a weak mechanical surface and low refractive index [41, 42].

Furthermore, PMMA is well tolerated by living tissue. Its rate of degradation in living organism is very slow. At present, the polymer is mainly used as bone cement, although problems sometimes arise in such applications due to the toxicity of the monomeric methyl methacrylate [43]. PMMA resin has been widely used for light illuminating devices, signboards, construction and accessories because of its high transparency, high surface gloss and good thermal and mechanical properties [44, 45].

PMMA is widely used for biomedical implants, barriers, membranes, microlithography and optical applications. In fact, it was the first implanted biomedical polymer [46–49]. **Table 2.8** illustrates the properties of PMMA.

Table 2.8 Properties of PMMA			
Parameter	**Unit**	**Value**	**References**
Density	g cm^{-3}	1.19	[50]
Number average MW	–	6.4×10^3	[51]
Weight average MW	–	6.8×10^3	
Limiting oxygen index	–	0.173	[52]
T_g	°C	90–105	[11, 53]
Degree of polymerisation	–	66.5	[54]

2.2.3 Nylon

Nylon is a large-volume commercial polymer. It possesses good mechanical properties, exceptional chemical and solvent resistance, and is easy to fabricate and process. However, its impact strength is low, and it easily absorbs water, which deteriorates its mechanical properties and dimensional stability. The properties of Nylon are tabulated in **Table 2.9**.

Nylon has the advantages of strength, high service temperature and toughness. It is resistant to creep, abrasion and fatigue. It is used in self-lubricating bearings with excellent chemical resistance. However, it has a narrow processing window, is relatively high in cost and there are no transparent grades available. Nylon polymer Nylon 6,6 is the third largest volume material.

Table 2.9 Properties of Nylon			
Parameter	**Unit**	**Value**	**References**
Density	g cm^{-3}	1.14	[55]
Melt flow index	g/10 min	12.35	
Surface tension	mN m^{-1}	47.6	[56]
Concentration of amino end groups	mval kg^{-1}	45–47	
T_m	°C	265	[11]

2.2.4 Polycarbonate

Polycarbonate (PC) is the fourth largest volume material. It is an amorphous engineering thermoplastic with good thermal stability, transparency, impact resistance and the ability to be processed on conventional machinery. Its surface properties are important for many applications, including medical, optics and so on. **Table 2.10** illustrates the properties of PC.

PC is known as a transparent material with good impact and temperature resistance. It is more dimensionally stable than other commodity moulded materials. PC has excellent outdoor weather resistance, can be painted without pretreatment, and is suitable for solvent bonding, a common assembly technique. However, it is relatively high in cost, with a high processing temperature, has limited chemical resistance, and cannot pick up such fine surface details as some other polymers.

Table 2.10 Properties of PC

Parameter	**Unit**	**Value**	**References**
Density	g cm^{-3}	1.20	[57]
T_g	°C (linear)	148.5	[58]
	°C (branched)	151.9	
Melt density	g cm^{-3} at 275°C	1.07	[59]
T_m	°C	268	[60]

2.2.5 Polyesters

The family of polyesters comprises all polymers with ester functional groups in the polymer backbone. Polyesters were the first family of synthetic condensation polymers. Their connecting ester groups can be varied over an immensely broad range, making the polyesters a diverse group, with applications from labile biomedical matrices to liquid crystals, fibres and temperature-resistant performance materials [61, 62].

Polyesters can undergo changes to their chemical and physical structures. This can affect their degradability. Aromatic esters are readily hydrolysed. Bulky substituents adjacent to the ester group can retard hydrolysis by stearic hindrances. The T_g and T_m values provide a good indication of structure–morphology relationships. Increasing the length of the methylene repeat unit substantially reduces the glass transition temperature without affecting the crystallinity. Application in drug release systems requires good correlation between the glass transition temperature and the permeability of the polyesters [63].

2.2.5.1 Polyethylene Terephthalate

Polyethylene terephthalate (PET) is a commercially important polymer finding applications in films, fibres and moulding resins [64]. It is crystalline, tough and inelastic in nature. Its processing from molten mass is of great importance, with the crystallisation processes from melt playing a significant role. Crystallisation is initiated by nuclei forming during the process of heterogeneous nucleation [65–67]. The structure of PET is presented in **Figure 2.3**. The properties of PET are listed in **Table 2.11**.

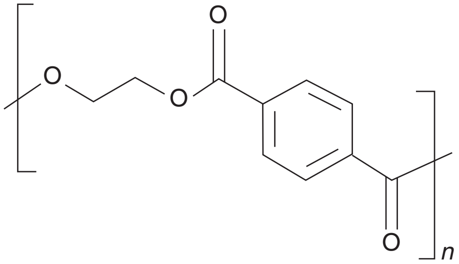


Figure 2.3 Structure of PET

Table 2.11 Properties of PET

Parameter	Unit	Value	References
Density	g cm^{-3}	1.41	[68]
Oxygen index	–	17	[69]
T_m	°C	247	[70]
Crystalline temperature	°C	126	
Crystallinity	%	24.4	
T_g	°C	78.5	[71]

2.2.5.2 Unsaturated Polyester Resins

Unsaturated polyester resins (UPR) form the bulk of all resins used for laminating applications. The basic materials used to make a polyester resin are a dibasic organic acid or anhydride and a dihydric alcohol. A portion of the dibasic acid is unsaturated, through which crosslinking occurs.

Although UPR show considerable utility in the composite industries, expansion into potentially high-volume applications has been restricted by a number of problems, including a poor surface appearance, fibre pattern showing at the surface, warpage of moulded parts, inability to mould close tolerances, and internal cracks and voids, particularly in thick sections such as reinforcing ribs and bosses [72].

2.3 Thermoset Polymeric Materials

For thermoset polymeric materials, the chemical reaction involved in their preparation is not complete when producing the moulding powder (which is still thermoplastic). By applying heat and pressure, the powder can be readily pressed into a mould to a desired shape. When the heated mould reaches the proper temperature, the chemical reaction is completed, with the creation of an infusible, crosslinked product. Being crosslinked, recycling of the material is not possible.

2.3.1 Phenol Formaldehyde

Phenol formaldehyde resins were among the first completely synthetic polymers made [73]. They have found wide commercial application due to their ablative properties, with potential use as high-temperature polymers [74, 75]. Phenolics were among the first synthetic polymers to be filled with fillers such as cotton fibres.

Phenol formaldehyde resin is usually synthesised by the condensation of phenol with formaldehyde. The product that is formed as a result of the polymerisation reaction is primarily dependent on the types of catalyst and the mole ratio of the reactants. In the present research work, phenol-formaldehyde resin has been synthesised by the reaction of phenol with formaldehyde in the ratio of 1:1.5. A basic catalyst, sodium hydroxide, is added to initiate and orient the addition reactions of formaldehyde on phenolic compounds. The catalyst in the reaction medium is hydroxide anion obtained from the sodium hydroxide. The OH- anion contributes to the formation of phenates by abstracting the alcoholic proton. Compared to the original phenol, the resulting *o*- and *p*-phenols are more reactive towards formaldehyde. They further react with formaldehyde, resulting in the formation of di- and trimethylol derivatives. This polymerisation reaction is repeated, resulting in the formation of trinuclear phenols from the binuclear phenol. It has been observed that further heating these initial products results in condensation and an increase in MW. Condensation takes place between the methylol groups to form a methylene ether link or between a methylol group and an active *ortho* and *para* hydrogen atom to yield a methylene link. It has been observed that the rate of heating determines the final product. Furthermore, the product formed during the polymerisation reaction between phenol and formaldehyde in the presence of alkali is a complex mixture of mono- and polynuclear phenols, in which the phenolic nuclei are linked by methylene groups.

2.3.2 Epoxy Resins

Epoxy resins are widely used in fibre-reinforced composites due to their superior thermal, mechanical and electrical properties. Depending on the chemical compositions and curing kinetics, mechanical properties such as adhesive strength, chemical resistance, heat resistance and electrical resistance vary, ranging from extremely flexible to having high strength and hardness. However, brittleness, delamination and fracture toughness limitations restrict its use in high-performance applications. Improved high-performance composites based on thermosetting polymers can only be achieved by simultaneously improving the resin, fibre and interface properties [76–79].

2.4 Summary

- Polymers can replace conventional materials due to their ease of processing.
- Polymers are economical for the production of end-use products.
- Polymers are classified as thermoplastics and thermosets.
- Thermoplastic polymer materials can be reprocessed.
- Thermoset polymeric materials include crosslinking and cannot be reprocessed.

References

1. T.K. Shin, J.H. Kim, and H.J. Choi, *Journal of Polymer Science*, 2000, 77, 1348.

2. J.M. Goddard and J.H. Hotchkiss, *Progress in Polymer Science*, 2007, **32**, 698.

3. L. Lin and A.S. Argon, *Journal of Materials Science*, 1994, **29**, 204.
4. M.A. Kenedy, A.J. Peacock and L. Mandelkern, *Macromolecules*, 1994, **27**, 5297.
5. N. Brown and I.M. Ward, *Journal of Materials Science*, 1983, **18**, 1405.
6. R.F. de Souza and O.L. Casagrande, Jr., *Macromolecular Rapid Communications*, 2000, **22**, 1293.
7. Z.J.A. Komon and G.C. Bazan, *Macromolecular Rapid Communications*, 2001, **22**, 467.
8. J.J.M. Cormont, *Advances in Polymer Technology*, 1985, **5**, 3, 209.
9. S.M. Tamboli, S.T. Mhaske and D.D. Kale, *Journal of Applied Polymer Science*, 2004, **91**, 110.
10. M. Lazár, A. Kleinová, A. Fiedlerová, I. Janigová and E. Borsig, *Journal of Polymer Science, Part A: Polymer Chemistry Edition*, 2000, **42**, 675.
11. P.G. Edgerley, *Plastics and Rubber Processing and Applications*, 1981, **1**, 1, 81.
12. Md. N. Islam, Md. M. Haque and Md. M. Huque, *Industrial & Engineering Chemistry*, 2009, **48**, 10491.
13. L. Rosik and F. Vecerka in *Styrene-based Plastics and Their Modification*, Eds., P. Svec, L. Rosik, Z. Horak and F. Vecerka, Ellis Horwood, New York, NY, USA, 1990, p.19.
14. D.L. Kaplan, R. Hartenstein and J. Sutter, *Applied and Environmental Microbiology*, 1979, **38**, 551.

15. J.E. Guillet, P.W. Regulski and T.B. Maneney, *Environmental Science & Technology*, 1974, **8**, 923.

16. G.J. Griffin, *Advances in Chemistry Series*, 1974, **134**, 159.

17. R.N. Work and Y.M. Trehu, *Journal of Applied Physics*, 1956, **27**, 1003.

18. S. Rastogi, J.G.P. Goossens and P.J. Lemstra, *Macromolecules*, 1998, **31**, 2983.

19. S. Saikrasun, P. Limpisawasdi and T. Amornsakchai, *Journal of Polymer Research*, 2009, **16**, 443.

20. L. Rosik and F. Vecerka in *Styrene-based Plastics and Their Modification*, Eds., P. Svec, L. Rosik, Z. Horak and F. Vecerka, Ellis Horwood, New York, NY, USA, 1990, p.109.

21. J.M.G. Cowie, D.J. Worsfold and S. Bywater, *Transactions of the Faraday Society*, 1961, **57**, 705; and A.F. Sirianni, D.J. Worsfold and S. Bywater S, *Transactions of the Faraday Society*, 1959, **55**, 2124.

22. L. Junggren, *Artificial Organs*, 1989, **8**, 9.

23. R.J. Jagar and R.J. Rubin, *Science*, 1970, **170**, 460.

24. N.D. Bort, V.G. Marinin, A.Y.A. Kalinin and V.A. Kargin, *Vysokomolekulyarnye Soedineniya*, 1968, **10**, 2574,

25. L.C. Uitenham and P.H. Geil, *Journal of Macromolecular Science, Part B: Physics*, 1981, **B20**, 593.

26. A.A. Tseng, M.A. Borrosky, S.M. O'Connor and J.J. Knotts, *Advances in Polymer Technology*, 1990, **10**, 3, 205.

27. M. Okada, *Progress in Polymer Science*, 2002, **27**, 87.

28. D. Cava, E. Giménez, R. Gavara and J.M. Lagaron, *Journal of Plastic Film and Sheeting*, 2006, **22**, 265.

29. S.G. Lee, E.Y. An, J.B. Lee, J.C. Park, J.W. Shin and G.K. Kim, *Surface and Coatings Technology*, 2007, **201**, 5128.
30. J. Kopećek and K. Ulbrich, *Progress in Polymer Science*, 1983, **9**, 1.
31. A.H. Kehayoglou, *European Polymer Journal*, 1983, **19**, 3, 183.
32. I. Engelberg and J. Kohn, *Biomaterials*, 1991, **12**, 292.
33. S. Wang, W. Cui and J. Bei, *Analytical and Bioanalytical Chemistry*, 2005, **381**, 547.
34. L.S. Nair and C.T. Laurencin, *Progress in Polymer Science*, 2007, **32**, 762.
35. J-M. Raquez, R. Narayan and P. Dubois, *Macromolecular Materials and Engineering*, 2008, **293**, 447.
36. B.L. Dickinson, *Journal of Biomaterials Applications*, 1988, **3**, 605.
37. J.B. Adeniyi, *European Polymer Journal*, 1984, **20**, 291.
38. M.D. Wolkowicz and S.K. Gaggar, *Progress in Polymer Science*, 1981, **21**, 9, 571.
39. J.D. Moore, *Composites*, 1973, **4**, 3, 118.
40. Y. Fu, J. Wang, G. Zhao, Y. Wang and S. Chen, *Journal of Applied Polymer Science*, 2011, **122**, 12.
41. A. Bürgel, W. Kleemann, M. Biebricher and H. Franke, *Applied Physics A: Material Science and Processing*, 1995, **60**, 5, 475.
42. N. Tsutsumi, T. Ono and T. Kiyotsukuri, *Macromolecules*, 1993, **26**, 20, 5447.

43. U. Borchard in *Systematic Aspects of Biocompatibility*, Ed., D.F. Williams, CRC Press, Boca Raton, FL, USA, 1981 and G.H. Burnett and G.L. Duncan, *Makromolekulare Chemie*, 1962, **51**, 154.

44. H.M. Jeong and Y.T. Ahn, *Macromolecular Research*, 2005, **13**, 102.

45. K.C. Lee and S.Y. Lee, *Macromolecular Research*, 2007, **15**, 244.

46. J.B. Park and R.S. Lakes in *Biomaterials: An Introduction*, Plenum Press, New York, NY, USA, 1992.

47. *Molecular Engineering of Ultrathin Films*, Eds., P. Stroeve and E.I. Franses, Elsevier, London, UK, 1987.

48. *Langmuir – Blodgett Films*, Ed., G.G. Roberts, Plenum Press, New York, NY, USA, 1990.

49. S.W. Kuan, C.W. Frank, Y.H. Lee, T. Eimori, D.R. Allee, R.F.W. Pease and R. Browning, *Journal of Vacuum Science & Technology B*, 1989, **7**, 1745.

50. J. Reignier and B.D. Favis, *Macromolecules*, 2000, **33**, 6998.

51. S.R. Tatro, G.R. Baker, K. Bisht and J.P. Harmon, *Polymer*, 2003, **44**, 167.

52. E. Devaux and C. Caze, *Composites Science and Technology*, 1999, **59**, 459.

53. C.M. Gomez and C.B. Buchall, *Polymer*, 1993, **34**, 21, 11; and E.M. Woo and M.N. Wu, *Polymer*, 1996, **37**, 2, 485.

54. J C. Vogl, T. Kitayama and O. Vogl, *Progress in Polymer Science*, 1997, **22**, 201.

55. Z-B. Chen, T-S. Li, Y-L. Yang, Y. Zhang and S-Q. Lai, *Macromolecular Materials and Engineering*, 2004, **289**, 662.

56. J. Piglowski, I. Gancarz, M. Wlaźlak and H-W. Kammer, *Polymer*, 2000, **41**, 6813,

57. E. Fekete, E. Földes, F. Damsits and B. Pukánszky, *Polymer Bulletin*, 2000, **44**, 363.

58. J.H. Park, J.C. Hyun and W.N. Kim, *Macromolecular Research*, 2002, **10**, 3, 135.

59. T.A. Hogan, M.A. Spalding, K.S. Cho and C.C. Chung in *Proceedings of the ANTEC Conference*, San Francisco, CA, USA, Society of Plastics Engineers, Bethel, CT, USA, 2002.

60. O.S. Carneiro, J.A. Covas, C.A. Bernardo, G. Caldeira, F.W.J. Van Hattum, J-M. Ting, R.L. Alig and M.L. Lake, *Composites Science and Technology*, 1998, **58**, 401.

61. W.H. Carothers, *Journal of the American Chemical Society*, 1929, **51**, 1929.

62. W.H. Carothers and G.A. Arvin, *Journal of the American Chemical Society*, 1929, **51**, 2560.

63. C.G. Pitt, T.A. Marks and A. Schindler in *Controlled Release of Bioactive Materials*, Ed., R. Baker, Academic Press, New York, NY, USA, 1980, p.19.

64. R.W. Stackman, *Industrial and Engineering Chemistry Product Research and Development*, 1982, **21**, 328.

65. *Nucleation*, Ed., A.C. Zettlemoyer, Marcel Dekker, New York, NY, USA, 1969.

66. E.P. Price, *Journal of Polymer Science, Part C: Polymer Symposia*, 1963, **3**, 117.

67. B. Wunderlich in *Macromolecular Physics*, Volume 2, Academic Press, New York, NY, USA, 1976.

68. S. Saikrasun, P. Limpisawasdi and T. Amornsakchai, *Journal of Polymer Research*, 2009, **16**, 443.

69. R.W. Stackman, *Industrial and Engineering Chemistry Product Research and Development*, 1982, **21**, 2, 330.

70. N.K. Kalfoglou, D.S. Skafidas, J.K. Kallitsis, J-C. Lambert and L.V. Stappen, *Polymer*, 1995, **36**, 23, 4453.

71. G. Wei, L. Wang, G. Chen and L. Gu, *Journal of Applied Polymer Science*, 2006, **100**, 1511.

72. K.E. Atkins in *Polymer Blends*, Volume 12, Eds., D.R. Paul and S. Newman, Academic Press, New York, NY, USA, 1978, p.391.

73. J. Gillis and R.E. Oesper, *Journal of Chemical Education*, 1964, **41**, 224.

74. A.A.K. Whitehouse, E.G.K. Pritchett and G. Barnett in *Phenolic Resins*, Iliffe, London, UK, 1967, Chapter 2.

75. C.L. Segal in *High Temperature Polymers*, Marcel Dekker, New York, NY, USA, 1967, p.147.

76. J. Kong, R. Ning and Y. Tang, *Journal of Materials Science*, 2006, **41**, 1639.

77. S. Kar and A.K. Banthia, *Journal of Applied Polymer Science*, 2005, **96**, 2446.

78. A.R. Siebert in *Proceedings of the 186th Meeting of the ACS on Rubber Modified Thermoset Resins*, American Chemical Society, Washington, DC, USA, 1984, p.179.

79. H. Dodiuk, S. Kenig, I. Blinsky, A. Dotan and A. Buchman, *International Journal of Adhesion and Adhesives*, 2005, **25**, 211.

3

Polymer and Additives

Additives, when added to polymers, help in their processing. The performance requirements of additives in a product result in a cost advantage that can only be realised when additives are used in the formulation. However, it is necessary to pay increased attention to the quality control of incoming raw materials. The compounding technique should be determined by weighing the advantages of overall cost savings against the disadvantages of having greater inventories, and the increased likelihood of additive cross-contamination in the blended compound.

3.1 Classification of Additives

Polymer additives can be classified on the basis of the improvement in properties and use throughout an application:

- Ageing and degradation:
    - Stabilisers (thermal stabilisers, antioxidant and light stabilisers)
    - Flame retardants
    - Smoke suppressants
- Physical properties modification:
    - Plasticisers
    - Lubricants

  - Nucleating agents
  - Processing aids
  - Mould-release agents
  - Curing agents

- Surface properties modification:

  - Slip additives
  - Antistatic agents
  - Antifogging agents
  - Coupling agents
  - Antimicrobial agents

- Economics:

  - Foaming agents
  - Fillers and reinforcements
  - Pigments
  - Colorants

3.2 Ageing and Degradation

3.2.1 Stabiliser

Thermal degradation occurs in polymers as a result of the high temperature required for their processing. Indeed, the degradation due to heat, oxidation and light during processing leads to a requirement for thermal stabilisers, anti-oxidants and light stabilisers, respectively.

3.2.1.1 Thermal Stabiliser

Polymers are subject to unsaturation, which leads to a colour change during processing, as a result of temperature and pressure [1, 2]. The use of stabilisers should ensure adequate stability of polymers during processing. Repeated processing with additional heat steps leads to a degree of unsaturation and a predictable decrease in the remaining thermal stability. The use of stabilisers is mandatory in order to guarantee long-term performance.

Thermal stabilisers such as lead salts, metal soap, organotin compounds or a mixture of metal salts or soaps and auxiliary thermal stabilisers help in processing polyvinyl chloride (PVC), which is otherwise unstable as a consequence of its processing temperature [3]. Use of one of these stabilisers works by replacing labile chlorine atoms in the PVC or by reacting with the hydrogen chloride generated during processing as a result of degradation [4].

Zinc and the calcium salts of stearic acid are used as low-toxic-hazard thermal stabilisers in PVC compounding [5]. The concentration of stearates greatly increases with the pH of the melt during processing. In foam PVC processing, with sodium bicarbonate as the foaming agent, the pH ranges from 7 to 8.5 and the stearate concentration is high [6], and the zinc and calcium salts of stearic acid have to be replaced by other suitable stabilisers to avoid damage to the processing equipment. The thermal stabilisers therefore help to prevent damage to the equipment as a result of pressure and temperature. They also influence outdoor applications of products in terms of maintaining colour stability [7]. PVC, with its nitrile elastomer modifiers, requires a heat stabiliser, and the nitrile rubber requires an antioxidant. Mercaptide costabilisers not only act as a heat stabiliser for the PVC, but also react preferentially with the butadiene unsaturation of the nitrile copolymer with a large number of double bonds rather than the dehydrochlorinated segments of the PVC, preventing degradation during processing.

3.2.2 Antioxidants

Antioxidants are key ingredients in the compounding of polyethylene (PE) and polypropylene (PP) due to the limited stability of polyolefins to high temperatures and ultraviolet (UV) light [8].

3.2.2.1 Degradation

Polymers exposed to air undergo oxidative degradation. They are processed at high processing temperatures, which initiate thermal oxidative degradation and a loss of physical properties. Resistance to thermal oxidation is one factor directly determining the commercial success of any polymeric material. Degradation during both processing and actual service life may cause irreversible changes to the polymer backbone. This is reflected in a loss of physico-chemical properties. Inhibition of oxidation by molecular oxygen is important in polyolefins during processing and fabrication, as well as for its long-term stability.

In polymer stabilisation technology, the combination of antioxidants with other stabilisers produces a synergistic stabilising effect. Antioxidants are used in polymers at low concentration levels during compounding (<1%). Depending on usage, these help to determine the long-term stability of the polymer and consume antioxidants over time. Polyolefin stabilisation is carried out with antioxidants such as a phenolic antioxidant (a primary stabiliser/radical quencher) or dialkyl-dithio-propionate or *tris*-alkyl-phenyl-phosphite (a secondary stabiliser/hydroperoxide decomposer). Polyamides are also stabilised by antioxidants. However, dialkyl-dithio-dipropionates are not used because of their relative volatility and intrinsic lower resistance to thermohydrolysis during processing. The addition of small amounts of mixtures of copper acetate and potassium iodide is used with polyamide to enhance the efficiency of the antioxidant [9].

3.2.2.2 Ageing

Ageing of polymers leads to drastic changes to their physical and mechanical properties. Hindered phenols are the most important antioxidants for polyolefins. However, some of the transformation products from these antioxidants can lead to discoloration during service life. In PP, mixtures of phosphites, hindered phenols and lactones are widely used [10–13]. Hindered phenols are very effective long-term heat stabilisers [14]. Phenolic compounds are antioxidants that can react with peroxy radicals, chain radicals and hydroperoxide to produce inactive decomposition products [15].

3.2.2.3 Ultraviolet or Oxidation

Damage to a polymer initiated by UV or oxidation in general occurs *via* free radical reactions. Such free radical reactions begin with initiation, followed by propagation, where the radicals from the polymer rearrange and try to form more stable radicals, thereby propagating further initiation reactions until the product properties degrade or become useless for particular application (such as doors and windows for outdoor application). The addition of antioxidants or UV inhibitors will terminate the free radical reactions or at least prevent further propagation of the reaction. In **Figure 3.1**, a generic reaction is schematically illustrated, showing initiation, propagation and termination reactions during processing or in UV during ageing.

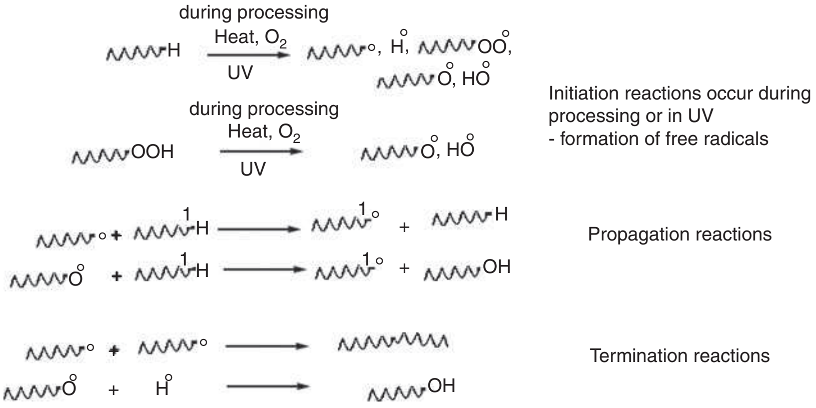


Figure 3.1 Chain reactions (initiation, propagation and termination): oxidative degradation during processing or in UV during ageing

Metal can also catalyse oxidation damage in a polymer. This depends upon the chemical structure of the polymeric material. Antioxidants either help to scavenge radicals or decompose peroxides or deactivate the metal that is catalysing the degradation. Additives that are not fully compatible with the polymer matrix may work very well as antioxidant/UV stabilisers, but will migrate out of the polymer over time (known as 'blooming'), thus making the polymer susceptible to damage.

Additives that are typically effective as antioxidants and UV stabilisers include hindered phenols, aromatic amines, hindered amines (only those that have a tendency to form N-oxides), hydroxylamines, benzofuranones, divalent sulfur compounds, phosphorus(III) compounds (phosphines and phosphites, with phosphites most common) and multidentate metal ligands (such as ethylenediaminetetracetic acid). Polymers to be processed above 300 °C are exceptions as there are no commercial antioxidants thermally stable enough to be processed at that temperature.

3.2.3 Light Stabilisers

For polymer materials – in terms of outdoor ageing – sunlight is the energetically most rich component of weather effects. Photochemical degradation causes a deterioration in mechanical characteristics. It induces cracking and eventually complete disintegration of the material. Polyolefins are more sensitive to irradiation than methods reflecting chemical changes [16]. Deterioration of mechanical properties is a final consequence of the series of processes involved in photochemical degradation.

For polyolefins, hindered amine-based on 2,2,6,6-tetramethylpiperidine derivatives are gaining importance as light stabilisers [14, 17]. They are effective as antioxidants at low and moderate temperatures [18]. Hindered amine light stabilisers have a synergistic effect in combination with aliphatic phosphites under photo-oxidative conditions [19].

UV degradation by light stabilisers can be achieved by:

- Reducing the chromophore groups present in the polymer chain. Additives simply known as UV absorbers include carbon black, iron oxide and soluble organic compounds such as hydroxybenzophenones and hydroxyphenylbenzotriazoles.
- Deactivating the excited species by energy transfer. These additives are known excited-state quenchers, typically nickel chelates of aromatic as well as aliphatic compounds.
- Scavenging the radicals to reduce the rate of propagation of auto-oxidation reactions. The additives are preferably hindered amines derived from piperidine.

3.2.4 Flame Retardants

Flame retardants prevent polymeric materials from supporting a flame, sufficiently to meet the requirements of standards. They are used either as additives mixed with the polymer or as coreactants, in which the reactive flame retardant is covalently bonded with the polymer. Polybrominated diphenyl ethers and organophosphate esters are both used as flame retardants as well as having plasticising properties. Tetrabromobisphenol A can be used either as an additive or as a reactive flame retardant [20].

PP has a high self-ignition temperature (570 °C), and during combustion has high flame and surface pyrolysis temperatures. It is therefore difficult to make flame retardants for it. Thermal degradation occurs at ~340 °C, which liberates a large amount of fuel into the flame. The crystallinity of PP may inhibit effective dispersion of additives such as flame retardants, reducing its effectiveness. PP requires flame retardants that act as inert fillers in the amorphous phase in order to minimise interfering with the properties of the final product. The synergism of antimony trioxide with halogen-bearing organics reacts in the molten polymer to form volatile halides or oxyhalides of antimony, which subsequently decompose to halides [21, 22]. The accelerating effects of different amines, ammonium salts and organophosphoric compounds such as phosphorus-containing organic substances provide surface-active properties or anti-ageing, or act as flame retardants or anti-reversing agents [23].

The chemistry of flame-retardant additives is highly varied and is optimised not only for specific polymer chemistries, but also to address flammability effects such as flame spread, dripping, smoke release and so on. Flame-retardant chemistry includes classes of compounds such as halogenated organics, char formers, crosslinking compounds, mineral fillers, intumescent packages, phosphorus compounds, nitrogen-based compounds and even certain metal and boron compounds.

This chapter cannot cover all the flame-retardant chemistries available, but they are extensively covered elsewhere in review books and articles [24–27]. **Figure 3.2** illustrates the difference in heat release by non-charring and charring polymers.

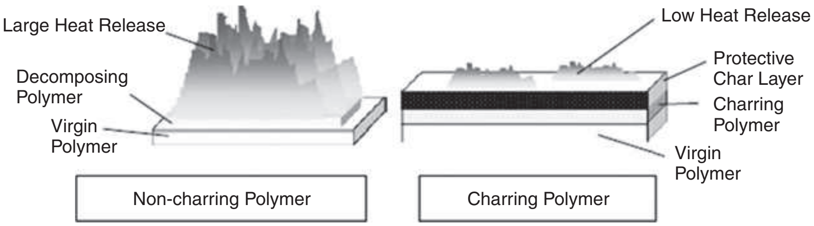


Figure 3.2 Differences in heat release from non-charring and charring polymers. Reproduced with permission from Dr. Jeffrey W. Gilman, US Department of Commerce, National Institute of Standards and Technology

3.2.5 Smoke Suppressants

To decrease smoke evolution, suitable smoke suppressants can be added that will reduce smoke generation during burning. PVC is intrinsically fire-retardant. However, if forced to burn it behaves like organic materials and produces smoke. Inert filler has no smoke-suppressant activity, but it reduces smoke by diluting the content of the compound with a non-flammable material. Non-flammable fillers can therefore help to decrease smoke generation [28].

Most smoke suppressants will not be useful in PVC compounds because of their higher cost, because they impart colour or are coloured, because discoloration occurs during processing, or they induce processing problems *via* thermal instability, UV instability and reduce physical properties.

3.3 Physical Properties Modification

3.3.1 Plasticisers

Plasticisers are known for their effectiveness in producing flexible polymers such as flexible PVC, acrylate copolymers and so on. Plasticisers are normally liquids, and are used in glassy polymers to reduce their glass transition temperature (T_g) with compatibility to avoid phase separation. Phase separation would cause migration to the surface. The rubbery effect results from the high levels of plasticiser bringing the T_g of the polymer to below room temperature. In semi-crystalline polymers, plasticisers would not only reduce the T_g of the amorphous domain but also decrease the melting point of the crystalline phase.

The application fields of plasticisers range from automobiles and construction to toys and medical products. Phthalate plasticisers such as dibutyl phthalate and di(2-ethylhexyl) phthalate are widely used due to the higher plasticising efficiency and lower volatility of these phthalate plasticisers. Phthalate plasticisers are still widely used in the processing of flexible PVC [29]. However, recently, the use of phthalate plasticisers has been questioned due to their debatable toxicity in consumer products made of PVC matrices, especially in blood supply and similar medical plastics, because the content of phthalate plasticisers in PVC-based medical plastics is in the range 10–80% [30–32].

Eco-friendly and non-toxic phthalate plasticisers, such as biodegradable tributyl citrate, triethyl citrate, acetyltributyl citrate, acetyltriethyl citrate and tri(2-ethylhexyl) citrate, have been widely used in the food and medical packaging fields [33–37].

3.3.2 Lubricants

Stearates or stearic acid can act as lubricants in PVC formulation. The migration of stearates occurs towards the surface [38, 39]. Wax is a well-known lubricant that is added to improve the processing of different polymers. It not only improves processing but also mechanical properties.

A low concentration of oxidised paraffin wax improves thermal stability [40], and unoxidised paraffin wax reduces thermal stability [41]. At higher wax concentrations in PVC, crystal phase separation as well as the presence of short wax chains in the amorphous fraction cause deterioration of thermal and mechanical properties.

Paraffin wax has been found to have an influence on the thermal and mechanical properties of low-density polyethylene (LDPE) [39, 40]. It crosslinks to improve the mechanical properties of LDPE, short sisal fibres composites [42, 43] and PVC. There is complete miscibility of the wax in LDPE at wax concentrations up to 10%, but only partial miscibility at higher wax concentrations. On blending an oxidised paraffin wax with LDPE, small wax concentrations improved the physical properties of the blends [40].

Lubricants are classified based on their actions with processing equipment and compounds, as described in the following sections.

3.3.2.1 Internal Lubricants

Internal lubricants typically reduce bulk viscosity by being partially compatible with the polymer, with the lubricant's soluble component helping to open the polymer chain, and the less soluble portion of the lubricant molecule providing intermolecular lubrication (e.g., fatty alcohols, esters, ethylene-vinyl acetate waxes). They promote flow with a reduction in die swell. In injection moulding, the provide improved weld line strength, clarity, die filling and rate of production. In extrusion it reduces head and back pressure while affecting paintability. However, an increase in internal lubricants lowers heat distortion.

3.3.2.2 External Lubricants

External lubricants typically provide lubrication between the polymer and the metal surface of the processing equipment, and include PE homo polymers, paraffins, esters, metallic soaps, amides, fatty acids and oxidised PE. In injection moulding they help with mould release and reduce the process temperature. However, an excess of external lubricants can promote plate out, cause delamination, lower weld line strength and cause surging with slow fusion.

In PVC, lubricants can drastically improve processing by preventing the polymer from sticking to the metal surface of the processing equipment. It reduces the internal friction of the polymer molecules. Lubricants improve the surface appearance of extrudates, depending on the compatibility with the resin. External lubricants have little compatibility with the polymer during processing, which affects fusion on the polymer. They reduce adhesion and sticking of the polymer in processing equipment. External lubricants reduce the internal friction between polymer aggregates. Internal lubricants have substantial compatibility. Internal lubricants promote fusion by reducing the internal friction of the molecules. An increase in external lubricants produces surging of extrudate, which makes it impossible to produce good parts. Excess internal lubricant creates back pressure in the equipment and may lead to degradation of the polymer. Some of the melting points of lubricants are shown in **Table 3.1**.

Common lubricants may be classified according to their chemical structures:

- Straight-chain carbon molecules such as paraffin waxes;
- Straight-chain molecules with end groups (e.g., monoglycerin esters or stearic acid); and
- Molecules with a polar centre with long carbon chains on each side (e.g., metal stearates).

Table 3.1 List of lubricants

Chemical name	**Approximate melting point (°C)**	**References**
Alkylated stearamide	144	[44, 45]
N,*N′*-ethylene bis(stearamide)	148	[46]
Paraffin – straight chain	74	
Barium stearate	165	
Cadmium stearate	140	
Hydroxyl stearic acid	78	
Lithium stearate	210	
Polyethylene wax	112	
Stearic acid	65	
Glyceryl esters of montanic acid (C_{28} – C_{32})	82	
Partially saponified montanic acid	100	

3.3.3 Nucleating Agents

Nucleating agents cause crystallisation, starting from a large number of small spherulites, which give rise to less light scattering and greater light transmission. They enhance the aesthetics *via* enhanced clarity and surface gloss. They also help to improve processing during injection moulding by reducing the cycle time and improving physical properties.

The addition of nucleating agents to a semi-crystalline polymer significantly affects the crystallisation behaviour and related morphology of the polymer. They provide additional nucleation sites, which are responsible for better crystallisation rates as well as the formation of small spherulites to improve the clarity of the polymer. Nucleating agents in PP improve clarity. Beyond a certain level of incorporation, the transparency reduces, with practically no further reduction in spherulite size. Dibenzylidene sorbitol, an organic nucleating agent, considerably improves the rate of crystallisation of PET [47–49]. The properties improved by nucleation include an increase in clarity, hardness, tensile strength and elasticity modulus [41].

3.3.4 Processing Aids

Acrylic process aids include copolymers of methyl methacrylate (MMA) and other types of acrylic monomers like ethyl acrylate, butyl acrylate and butyl methacrylate. Some even include styrene monomer, imparting to the polymer an antisticking effect due to its limited compatibility with PVC. The functions of these lubricating process aids are not described in this chapter.

A first important factor in the behaviour of process aids is the choice of comonomers and their polymerisation sequence. MMA offers excellent compatibility with wood composites (WC) but has a higher T_g. Acrylate monomers are less compatible but have much lower T_g than MMA. When combined with MMA in a process aid, they facilitate polymer sequences able to soften earlier than PVC, thus promoting fusion of the compound.

Process aids are obtained through emulsion polymerisation, a process able to lead to extremely high molecular weights (MW), often above 1 million, when compared with WC MW, which typically range from 50,000 to 65,000 for films and bottles, and from 60,000 to 80,000 for rigid extrusion.

PVC has also been used as a polymer matrix for some wood/plastic composites. The processing of wood-filled WC is rather challenging because of the high temperature increase due to shear heating, high melt viscosity and low melt strength, leading to poor extrusion quality. To overcome these difficulties, very high-MW process aids are beneficial. However, it has been proven that their chemical composition is a critical parameter, as some grades would tend to further increase temperatures and torques, while others, like Plastistrength 530, increase output and maintain low torques [50].

3.3.5 Mould-release Agents

The main problem of moulding with polymers is that the product often sticks in the mould. Deposits from previous items stick to the surface of the mould and cause surface defects on the next product. This reduces the production rate of the process. A mould-release agent is essential in the design and manufacture of any pre-shaped part. Release agents form microthin, thermally stable surfaces that are chemically bonded to the mould surface and allow the material to be released quickly and easily. A good mould-release agent results in multiple, contaminant-free releases, thereby reducing manufacturing costs, decreasing the downtime required for cleaning the mould and ensuring defect-free parts.

External mould releases are applied to the mould surface. They can be applied by hand or using spray equipment, a faster method. Their correct application is critical in ensuring their optimal performance.

Internal mould-release agents are combined with the resin prior to moulding. The product is dissolved in the resin mix, and therefore must be highly soluble in its own cycle (this is a continuous process in pultrusion). Internal release agents are commonly associated with mechanised processes, but they can also assist in difficult highly detailed hand lay-up mouldings. One major advantage of using this type of release agent is consistency, and in high-volume production where an externally applied release is used.

The desirable characteristics of release agents include the following:

- Odourless, with a short drying time and simple application procedure;
- Does not build up on the mould;
- Does not transfer onto moulded parts;
- Thermally stable even at high temperature, with multiple release properties; and
- Effects on environment and regulations related to health and safety.

3.3.6 Curing Agents

Curing agents are hardeners, which are chemically active compounds used to convert epoxy resins into hard and infusible thermosets. These agents promote the crosslinking reaction by self-polymerisation, without the formation of any by-product. Amines such as aromatic, aliphatic, cyclo-aliphatic amines are used as curing agents depending upon the property requirements and application.

A large group of curing agents comprises derivatives of ethylenediamine. Generally, aromatic amines such as 4,4′-diaminodiphenylmethane require higher curing temperatures than aliphatic amines such as the ethylenediamine derivatives, which cure the epoxy resin at room temperature. Among the cycloaliphatic amines, isophoronediamine is the most widely used. The hardeners used in cold curing are mostly polyamines, polyamides or isocyanates, and those used for thermal curing are carboxylic acids and anhydrides or aldehyde condensation products, e.g., phenol-formaldehyde resins, melamine-formaldehyde resins and urea-formaldehyde resins. Ideally, all epoxy groups of the epoxy resin have reacted when it is cured.

3.3.7 Slip Additives

Slip additives are incorporated directly into the polymer during the extrusion process. They work by migrating to the surface as the polymer cools, forming a solid lubricating layer at the surface, lowering the friction or reducing adhesion between contacting polymer surfaces and the polymer and other materials.

Erucamide and oleamide are the most commercially important slip additives. It is generally considered that oleamide blooms to the surface faster, thus providing quicker slip development. The advantages of erucamide over oleamide include lower volatility, superior colour and heat stability, improved organoleptic properties, better blocking performance over similar formulations containing oleamide, and a lower final coefficient of friction.

3.3.8 Antistatic Agents

Antistatic agents are amphiphilic molecules with a hydrophobic tail, which entraps into the polymer matrix, and a hydrophilic head, which migrates to the surface and absorbs a conductive layer of water. This absorbed water leaks the static charge formed on the plasticised PVC surface [51–53]. Such antistatic agents are easy to prepare and purchase, but their antistatic properties depend strongly on moisture and they do not have sufficient antistatic effect with low environmental humidity. Reducing the environmental humidity sensitivity of traditional antistatic agents is very important for their application under all environmental conditions.

Antistatic agents such as carbon black, metal powders, surfactants or other hydrophilic substances can be blended with polymer matrices to dissipate electronic charge. However, carbon black makes materials black, so if a light colour is required, carbon black cannot be used. If some low-MW antistatic agents like surfactant are used, their antistatic effect is brought about by the equilibrium moisture adsorbed on the surfactant, so sufficient antistatic effect is not achieved under low humidity. Furthermore, the surfactant is removed by rubbing or washing back and forth, and the antistatic effect disappears easily [54].

To solve these problems, many antistatic agents are incorporated into the polymer at the moulding process or applied to the surface of the products in a finishing process to control the surface resistivity of the moulded part to ~10^{11}–10^{8} Ω/sq [55–68].

One of the advantages of polymers is its inherent dielectric property, but this can be a problem when static electricity needs to be dissipated. Antistatic agents are described in **Sections 3.3.8.1** and **3.3.8.2**.

3.3.8.1 Internal Antistatic Agents

These are compounded in the polymer and migrate or bloom to the polymeric surface due to their incompatibility with the material.

3.3.8.2 External Antistatic Agents

These are applied to the surface of a polymeric material part. They are more effective but are short-lived. Dryer sheets increase the surface conductivity of polymer fabric, and the clothes lose their static charge.

3.3.8.3 Ion Dispersion Agents

These are developed for the electronics and packaging industries, which need short-term static discharge dissipation. The surface static charge of the polymers is temporarily neutralised by exposing the part to a slightly ionic atmosphere, the charge of which is opposite that of the polymeric part.

3.3.9 Antifogging Agents

The antifogging effect is a problem of the wettability of the polymer surface. Polymers can be modified by the addition of tensoactive agents (antifog additives). Antifog additives are used because of their low cost. Once incorporated with a polymer, they migrate in response to an increase in surface tension. A small quantity of additive dissolves in water droplets, decreasing the surface tension of the water. At a certain point, both surface tensions become similar and water spreads as a thin continuous layer that does not reflect the sunlight, in what is called the 'antifog' effect [59, 60].

Fogging forms small water droplets on the surface of polymer films. Hence, unwanted effects may result, leading to a reduction in clarity and dripping. The additives migrate on the surface of the polymer to achieve the antifogging property. Migration properties are critical parameters. Additives are continuously lost from the surface, as some dissolves in the surface water. It is therefore essential to use additives with suitable migration and low solubility in water to give rise to an adequate surface concentration for a maximum time period. It is necessary to know the type of polymer and the temperature at which the part is to be used before selecting the antifogging additive. An increase in additive size in PE films decreases the migration rate of the antifog additive. As the crystallinity of PE is increased, the migration rate of the additive to the surface increases [62–64].

Antifogging additives are typically surface-active product. They have a hydrophilic head and a lipophilic tail (such as sorbitan, glycerol, polyglycerol and polyoxyethylene esters). Antifogging agents eliminate the reduction of transparency by migrating to the surface and increasing the surface critical wetting tension of the polymer. Glycerol esters act as antifogging agents. They are useful in agricultural and packaging films, including food-wrapping films.

3.3.10 Coupling Agents

The concept of coupling agents is well known in the field of reinforced and filled plastics. Their main function is to overcome incompatibility between two phases. A coupling agent, usually a bifunctional molecule, is capable of forming covalent bonds with both the organic polymer matrix and the fibre or filler. The bonds across the interface between the polymer matrix and the reinforcement achieved *via* the coupling agent provide good adhesion, even under high humidity. This is required to obtain satisfactory long-term properties of composite materials [65].

Coupling agents act to adhere the polymer phase to the filler particle to improve mechanical properties. Coupling agents are low-MW substances. They still improve properties by strongly interacting with both the filler and the polymer matrix. The ideal coupling agent for use in filled polymer systems is a modified polymer containing some polar functionality. Several coupling agents have been used, including silanes, titanates, as well as functionalised PP, namely maleic anhydride or acrylic acid polymer [66–68].

Coupling agents promote adhesion between two dissimilar phases in composite materials. They are used in small quantities to modify a surface to create a better dispersion of the material and favour agglomerate breakdown. Silane coupling agents are the most commonly used inorganic material.

Adherence between the filler and polymer surfaces is improved using coating or wetting additives such as stearates, titanates or zirconates by improving the level of wetting of the filler by the polymer and then having two active surface parts. Coupling agents do not, however, increase the interfacial adhesion between the polymer and filler needed for sufficient stress transfer in the composite and to improve the dispersion of load in the polymer [69]. Such interfacial adhesion is needed to improve the physical properties in order to promote adhesion between the filler and polymer.

The application of coupling agents for the surface modification of fillers and reinforcements in polymers has generally been directed towards improving the mechanical strength and chemical resistance of composites by improving adhesion across the interface. Although adhesion is central to any ‘coupling’ mechanism, it is recognised that many factors are involved in the total performance of a composite system [70–72].

Coupling agents usually have a dual reactivity because they contain pendant groups capable of reacting both with the resin and with the filler surface. The stability of composites appears to be related to the strength of the covalent bonds between the resin and the filler *via* the coupling agent. Although the exact mechanism of bonding may still be controversial, we believe that the organofunctional portion of the coupling agent reacts with resins and becomes covalently bonded to the resin matrix.

The surface modification of the filler particles also affects the rheology (viscosity and elasticity) of the polymer by changing the dispersion of the particles [73, 74]. Coupling agents, designed to improve the coupling of the fillers to the resins, often improve the processability of filled polymeric materials, for instance, in compounding and injection moulding. However, much is lacking in our understanding of the role that coupling agents play in the improvement of processability.

3.3.11 Antimicrobial Agents

Polymers with antimicrobial activity are often required for food packaging, sanitary or medical applications. Those materials are usually prepared by the formulation of polymers with side groups with antimicrobial activity, which can be cleaved from the polymer matrix. Some azole compounds constitute versatile and valuable sources of antimicrobial agents. They appear to transcend the chemotherapeutic boundaries of other antiparasitic drugs with a spectrum of activity that includes the majority of fungi, as well as many bacteria, protozoa and even helminthic species.

Numerous antimicrobial agents such as quaternary ammonium salts, *N*-halamines, phosphonium salts, silver ions and natural bioactive agents have been utilised to impart antimicrobial properties to surfaces [75–79].

Antimicrobial agents are added to polymers to destroy microorganisms that cause mildew, objectionable odours or structural degradation. Because they are used to prevent odour, biocides also qualify as aesthetic property modifiers. Microbial attack commonly occurs with natural polymers, but synthetic polymers, particularly those prepared from alkenyl monomers, are often highly resistant. Additives such as plasticisers, however, promote biological action even on the more resistant polymers. Antimicrobial agents include inorganic compounds such as borax and copper(II) nitrate, metal naphthenates and such heterocyclic compounds as 2-mercaptobenzothiazole and its sodium or zinc salts. Antimicrobial agents used to prevent odour, primarily in PE bin bags and PVC, are generally organoarsenic and organoantimony compounds. The choice and concentration of biocide depends on the chemical makeup of the polymer and the polymer's use environment.

3.4 Economics

3.4.1 Foaming Agents

Both chemical and physical blowing agents (PBA) are used to expand extruded plastics. The choice of blowing agent depends somewhat on the product being made.

For example, in profile foam operations, where higher density foams are desired, it is general practice to use chemical blowing agents (CBA). These materials, which decompose under polymer melt processing conditions to yield gases to expand the polymer, are usually dry-blended with the resin and then fed to the extruder. They can also be compounded directly into the resin by the polymer supplier and provided as a ready-to-use masterbatch.

One processing shortcoming of CBA is that once a blend has been prepared, it is not possible to adjust the product density during foaming by changing the blowing agent concentration [80].

In its most general terms, the production of thermoplastic foams involves expansion of a gaseous phase dispersed throughout the polymeric melt. The gaseous phase may be generated from either a PBA or a CBA. CBA are solid or liquid materials that decompose under certain conditions to liberate gases [81]. Because gas generation from a CBA is generally thermally activated, CBA can be used either in a high-pressure foaming system, such as injection moulding and extrusion, or in an atmospheric pressure system, such as rotational foam moulding. It is believed that, when a CBA is adopted in a high-pressure foaming process, the vapour materials generated by decomposition of the CBA then behave like PBA [82]. However, unlike the PBA-based foaming processes, the nucleation mechanisms differ with a CBA, especially under atmospheric pressure.

3.4.2 Fillers and Reinforcements

The filler particles are more or less agglomerated. Agglomeration can have a very great effect on mechanical properties. Three characteristics of the filler phase in the polymer matrix are important in determining the dynamic mechanical properties of the composite: (1) the shape and state of agglomeration of the filler; (2) the maximum packing fraction of the filler, which is also determined by the particle shape and the state of agglomeration as well as by filler–polymer interactions; and (3) the mechanical strength of the agglomerates.

The beneficial effects of surface treatments of filler particles, including silane treatments, are generally attributed to improved adhesion of the polymer to the filler surface. However, it should be realised that in many cases the changes in the degree of agglomeration brought about by the surface treatments are equally, or more, important [83].

Temperatures do not depend on the amount or size of filler. The values of the bulk moduli and the thermal expansion coefficients are independent of filler size, but depend considerably on the volume fraction of filler. All filled and unfilled materials show a glass–rubber transition, at which temperature the thermal expansion coefficient increases considerably and the bulk modulus decreases sharply [84]. The mineral fillers seem to modify mechanical properties on three levels [85, 86]: in terms of their nature, their size, shape and distribution, and in terms of the changes they bring about in the microstructure of the matrix.

3.4.2.1 Calcium Carbonate

Calcium carbonate is one of the most used inorganic fillers in polymer processing. It is an engineered additive used to enhance properties. It does not just take up space, but acts as a processing aid in extrusion by increasing shear, and produces a compound with a higher modulus of elasticity that will reduce deflection in a gravity flow sewer pipe. Its unrestricted use would produce a tensile strength of less than 4,000 psi. At 30 parts per hundred, it contains approximately 11% by volume. It does reduce tensile strength, but does not influence deflection.

3.4.2.2 Reinforcements

Natural fibres are particularly used in the automotive industry, where a number of products can be produced by using natural fibres as reinforcement [87–89]. With regard to the environmental advantages, these biofibres are suitable alternatives to synthetic fibres as reinforcements in polymers [90, 91]. Synthetic fibres can cause health problems and are on the whole difficult to recycle. Composites made from either bioplastics or biofibre are called biocomposites [92, 93]. Current biofibre-reinforced polymer composites are being used because of their good mechanical properties, simplicity in fabrication, economy as well as other features [94, 95]. Thermosetting resins have the features of good processability, water resistance and chemical inertness. Mechanical properties such as tensile strength, compressive strength, flexural strength and wear resistance are greatly improved by reinforcement [96, 97].

3.4.3 Pigments

Pigments [98] are solid particles with size in the range of ~0.1–1 μm. They vary greatly in shape. They also have a narrow shape and particle size distribution, giving heat resistance, insolubility in solvents and binders, fastness to weathering and stability to UV light. The specific properties of a pigment determine its use as colorant or filler. They result from the interplay of solid-state properties such as particle size and morphology of the pigment. Typical solid-state properties include chemical composition and the structure of the solid, including colour, refractive index and so on.

Pigment properties are affected by particle size and shape, and include hue, light scattering and so on. The main factors are the dispersibility of the pigment and the stability of the dispersion. Pigments are used in a dispersed form [99, 100].

3.4.4 Colorants

Colorants are usually either an organic or inorganic dye or pigment. The amount of colorant added to polymeric materials is related to the colour of the base material. The colorant may be in the form of a powder, liquid or pellets. It is added as percentage by weight.

Colorants are classified into white pigments and coloured pigments. White pigments show no absorption in the visible range. However, coloured pigments absorb certain wavelengths in the visible region. The reasons for the colour reside in the molecule are attributable to charge transfer and the electronic transitions of visible light. The colour permits electron transitions between split energy levels as a result of light absorption in the visible range. The shape of the absorption spectrum is responsible for the purity of hue.

In the white pigment titanium dioxide (TiO_2), the particle sizes corresponding to this optimum are in the range from 0.15 to 0.25 μm. This is because, for TiO_2, the scattering maxima for the wavelengths of white light lie in this range.

3.5 Summary

- Additives added to a polymer do not form primary chemical bonds intentionally.
- Migration towards the surface can modify surface properties.
- Lack of control of polymer surface composition leads to important problems, with economic consequences.
- Additives not chemically bound to the polymer matrix may leach out into the environment at any time during the production, lifetime or destruction of a product.
- Additives help the polymer to survive the processing used to transform it into the desired shape.

References

1. A. Shaidleb, *Journal of Vinyl & Additive Technology*, 1979, 2, 1.
2. R. Brown, *Journal of Vinyl & Additive Technology*, 1981, 2, 3.

3. M. George in *PVC: Production, Properties and Uses*, The Institute of Materials, London, UK, 1996.
4. Y.B. Liu, W.Q. Liu and M.H. Hou, *Polymer Degradation and Stability*, 2007, **92**, 1565.
5. G. Smistad, T. Waaler and P.O. Rooksvaag, *Acta Pharamaceutica Nordica*, 1989, **1**, 287.
6. F. Galavotti, inventor; Hopsal AG, assignee; EP0635255A1, 1995.
7. J.D. Isner and J.W. Summers, *Polymer Engineering & Science*, 1978, **18**, 905.
8. S. Al-Malaika, *Advances in Polymer Science*, 2004, **169**, 121.
9. K. Schwarzenbach in *Plastics Additives Handbook*, Eds., R. Gachter and H. Miiller, Hanser Publishers, Munich, Germany, 1987.
10. W.O. Drake, J.R. Pauquet, R.V. Todesco and H. Zweifel, *Angewandte Makromolekulare Chemie*, 1990, **176/177**, 215.
11. H. Zweifel in *Degradation, Stabilization, and Lifetime Prediction*, ACS Advances in Chemistry No. 249, Eds., R.L. Clough, N.C. Billingham and K.T. Gillen, American Chemical Society, Washington, DC, USA, 1996, p.375.
12. P. Nesvadha and C. Krõhnke in *Proceedings of the 6th Additives '97 International Conference*, New Orleans, LA, USA, ECM Inc., Plymouth, MI , USA, 1997.
13. D. Mũller, *Kunststoffe*, 1998, **88**, 1212.
14. H. Zweifel in *Stabilization of Polymeric Materials*, Springer, Berlin, Germany, 1998.

15. G. Heinrich, M. Klüppel and T.A. Vilgis, *Current Opinion in Solid State & Materials Science*, 2002, **6**, 195.
16. J. Pabiot and J. Verdu, *Polymer Engineering & Science*, 1981, **21**, 32.
17. F. Gugumus, *Polymer Degradation and Stability*, 1989, **24**, 289.
18. W.O. Drake in *Proceedings of the 14th International Conference on the Advance in the Stabilization and Degradation of Polymers*, Luzern, Switzerland, Taylor & Francis, London, UK, 1992.
19. I. Bauer, W.D. Habicher, S. Korner and S. Al-Malaika, *Polymer Degradation and Stability*, 1997, **55**, 217.
20. *Environmental Health Criteria 172: Tetrabromobisphenol A and Derivatives*, International Program on Chemical Safety, World Health Organization, Geneva, Switzerland, 1995.
21. R.J Schwarz in *Flame Retardancy of Polymeric Materials*, Volume 2, Eds., W.C. Kuryla and A.J. Papa, Marcel Dekker, NY, USA, 1973, Chapter 2.
22. J.J. Pitts, P.H. Scott and D.G. Powell, *Journal of Cellular Plastics*, 1970, **6**, 35.
23. T.G. Vladkova, *Polymer International*, 2004, **53**, 844.
24. *Fire Retardancy of Polymeric Materials*, 2nd Edition, Eds., C.A. Wilkie and A.B. Morgan, CRC Press, Baco Raton, FL, USA, 2009.
25. *Advances in Fire Retardant Materials*, Eds., A.R. Horrocks and D. Price, Woodhead Publishing, London, UK, 2008.

26. E.D. Weil and S.J. Levchik, *Journal of Fire Sciences*, 2004, **22**, 339; and S. Bourbigot and S. Duquesne, *Journal of Materials Chemistry*, 2007, **17**, 2283.

27. *Fire Properties of Polymer Composite Materials*, Eds., A.P. Mouritz, and A.G. Gibson, Springer-Verlag, Amsterdam, The Netherlands, 2006.

28. W.J. Kroenke, *Journal of Applied Polymer Science*, 1981, **26**, 1167.

29. J. Murphy in *Additives for Plastics Handbook*, 2nd Edition, Elsevier, New York, NY, USA, 2001.

30. J.A. Tickner, T. Schettler, T. Guidotti, M. McCally and M. Rossi, *American Journal of Industrial Medicine*, 2001, **39**, 100.

31. *Plastics Additives and Modifiers Handbook*, Ed., J. Edenbaum, Van Nostrand Reinhold, New York, NY, USA, 1992.

32. *International Plastics Handbook*, 3rd Edition, Eds., J. Haim and D. Hyatt, Hanser, New York, NY, USA, 1995.

33. N. Ljungberg and B. Wesslen, *Polymer*, 2003, **44**, 7679.

34. S. Wong, R.A. Shanks and A. Hodzic, *Polymer Engineering & Science*, 2003, **43**, 1566.

35. M. Erceg, T. Kovacic and I. Klaric, *Polymer Degradation and Stability*, 2005, **90**, 313.

36. H. Kranz, N. Ubrich, P. Maincent and R. Bodmeier, *Journal of Pharmaceutical Sciences*, 2000, **89**, 1558.

37. H.M. Park, X.M. Liang, A.K. Mohanty, M. Misra and L.T. Drzal, *Macromolecules*, 2004, **37**, 9076.

38. E.B. Rabinovitch, E. Lacatus and J.W. Summers, *Journal of Vinyl & Additive Technology*, 1984, **26**, 351.
39. E.A. Collins, T.E. Fahey and A.J. Hopfinger, *Polymer Science and Technology*, 1984, **26**, 351.
40. V. Djokovic, T.N. Mtshali and A.S. Luyt, *Polymer International*, 2003, **52**, 999.
41. T.N. Mtshali, I. Krupa and A.S. Luyt, *Thermochimica Acta*, 2001, **380**, 47.
42. K. Joseph, S. Thomas and C. Pavirthran, *Polymer*, 1996, **37**, 5139.
43. M.A. Mokoena, V. Djokovic and A.S. Luyt, *Journal of Materials Science*, 2004, **39**, 10, 3403.
44. B.I. Marshall, *British Plastics,* 1969, **42**, 70.
45. U. Jacobsen, *British Plastics,* 1961, **34**, 328.
46. J.E. Hartitz, *Polymer Engineering Science*, 1974, **14**, 392.
47. H.N. Beck, *Journal of Applied Polymer Science*, 1967, **11**, 673.
48. G. Groeninckx, H. Berghmans, N. Overbergh and G. Smets, *Journal of Polymer Science, Part B: Polymer Physics Edition*, 1974, **12**, 303.
49. S.N. Garg, R.S. Stein, T.K. Su, R.J. Tabar and A. Misra in *Kinetics of Aggregation and Gclation*, Eds., D.P. Landan and F. Family, Amsterdam, The Netherlands, 1984, p.229.
50. I.J. Jansen in *Plastics Additives Handbook*, 3rd Edition, Eds., E. Gachter and H. Mtiller, Hanser Publishers, New York, NY, USA, 1990.

51. B. Azimipour and P. Schipper in *Acrylic Processing Aids: Keys to the Future*, SPE Vinyltec, Society of Plastics Engineers, Bethel, CT, USA, 2002, p.337.

52. C.G. Markus, *Plastics, Additives and Compounding*, 1999, **89**, 20.

53. E. Doris, *Additives*, 1999, **7**, 28; and R.F. Grossman, *Journal of Vinyl & Additive Technology*, 1993, **15**, 164.

54. F. Jonas and K. Lerch, *Kunststoffe/ Plast Europe*, 1997, **87**, 48.

55. L. Crisci, C.D. Volpe, G. Nese and R. Palumbo, *Macromolecular Bioscience*, 2003, **3**, 749.

56. T. Kobayashi, B.A. Wood, A. Takemura and H. Ono, *Polymer Engineering & Science*, 2008, **48**, 2247.

57. S. Monte, *Polymers & Polymer Composites*, 2002, **10**, 1.

58. C. Qiu, J. Wang, S. Mao and W. Guo, *Polymers for Advanced Technologies*, 2009, **20**, 702.

59. S. Gupta, R. Ou and R.A. Gerhardt, *Journal of Electronic Materials*, 2006, **35**, 224.

60. J.A. Howarter and J.P. Youngblood, *Macromolecular Rapid Communications*, 2008, **29**, 4551.

61. E. Espí, A. Salmerón, A. Fontecha, Y. García and A.I. Real, *Journal of Plastic Film and Sheeting*, 2006, **22**, 851

62. E. Földes, *Die Angewandte Makromolekulare Chemie*, 1998, **261/262**, 65.

63. K. Lee, K. Cho, I. Park, B.H. Lee, D. Rana and S. Choe, *Journal of Polymer Science, Part B: Polymer Physics Edition*, 1999, **37**, 1387.

64. A. Jaffrin and J. Guion, *Plasticulture*, 1994, **102**, 41.

65. E. Földes and A. Szigeti-Erdei, *Journal of Vinyl & Additive Technology*, 1997, **3**, 220.

66. E.P. Plueddemann in *Silane Coupling Agents*, Plenum Press, New York, NY, USA, 1982.

67. J. Kolarick, F. Lednicky, J. Jancar and B. Pukansky, *Polymer Communications*, 1990, **31**, 201.

68. D.J. Olsen and K. Hyche, *SPE ANTEC Preprints*, Society of Plastics Engineers, Bethel, CT, USA, 1989, p.1375.

69. K.A. Borden, R.C. Weil and C.R. Manganaro, *SPE ANTEC Preprints*, Society of Plastics Engineers, Bethel, CT, USA, 1993, p.2167.

70. A. Adur, R. Constable and J. Hurnenick, *SPE ANTEC Preprints*, Society of Plastics Engineers, Bethel, CT, USA, 1988, p.1474.

71. E.P. Plueddemann in *Interfaces in Polymer Matrix Composites*, Ed., E.P. Plueddemann, Academic Press, New York, NY, USA, 1974, Chapter 6.

72. M.W. Ranney, S.E. Berger and J.G. Marsden in *Interfaces in Polymer Matrix Composites*, Ed., E.P. Plueddemann, Academic Press, New York, NY, USA, 1974, Chapter 5.

73. E.P. Plueddemann and G.L. Stark in *Proceedings of the SPI 32nd Annual Technical Conference*, Reinforced Plastics/Composites Institute, The Society of the Plastics Industry, New York, NY, USA, 1977, 4C.

74. M.S. Boaira and C.E. Chaffey, *Polymer Engineering & Science*, 1977, **17**, 715.

75. C.D. Han, C. Sandford and H.J. Yoo, *Polymer Engineering & Science*, 1978, **18**, 849.

76. G. Sun and S. Worley, *Journal of Chemical Education*, 2005, **82**, 60.

77. G. Sun, X. Xu, J. Bickett and J. Williams, *Industrial & Engineering Chemistry*, 2001, **40**, 1016.

78. V. Sambhy, B. Peterson and A. Sen, *Langmuir*, 2008, **24**, 7549.

79. H. Haufe, K. Muschter, J. Siegert and H. Böttcher, *Journal of Sol-Gel Science and Technology*, 2007, **45**, 97.

80. V. Sambhy, M. Macbride, B. Peterson and A. Sen, *Journal of the American Chemical Society*, 2006, **128**, 9798.

81. L.I. Naturman, *Plastics Technology*, 1969, **15**, 10, 41.

82. J.L. Throne in *Thermoplastic Foams*, Sherwood Technologies, Sherwood Publishers, Hinckley, OH, USA, 1996.

83. T. Pontiff in *Foam Extrusion: Principles and Practice*, Ed., S.T. Lee, Technomic, Lancaster, PA, USA, 2000, p.251.

84. L.E. Nielsen, *Journal of Polymer Science, Part B: Polymer Physics Edition*, 1979, **17**, 1897.

85. C.W. van der Wal, H.W. Bree and F.R. Schwarzl, *Journal of Applied Polymer Science*, 1965, **9**, 2143.

86. L. Averous, J.C. Quantin, D. Lafon and A. Crespy, *International Journal of Polymer Analysis and Characterization*, 1995, **1**, 339.

87. L. Averous, J.C. Quantin, D. Lafon and A. Crespy, *Acta Stereologica*, 1995, **14**, 1, 69

88. A.S. Singha and V.K. Thakur, *International Journal of Polymeric Materials and Polymeric Biomaterials*, 2009, **58**, 1, 1.

89. A.S. Singha and V.K. Thakur, *International Journal of Polymeric Materials and Polymeric Biomaterials*, 2008, **57**, 12, 1059.

90. A.S. Singha and V.K. Thakur, *e-Journal of Chemistry*, 2008, **5**, 4, 1055.

91. A.S. Singha and V.K. Thakur, *Iranian Polymer Journal*, 2008, **17**, 7, 782.

92. A.S. Singha and V.K. Thakur, *Bioresources*, 2008, **3**, 4, 1173.

93. A.S. Singha and V.K. Thakur, *Polymer-Plastics Technology and Engineering*, 2009, **48**, 2, 201.

94. A.S. Singha and V.K. Thakur, *Bulletin of Materials Science*, 2008, **31**, 1, 7.

95. A.S. Singha and V.K. Thakur, *Polymer Composites*, 2009, **17**, 3, 127.

96. A.S. Singha and V.K. Thakur, *Journal of Polymer Materials*, 2009, **26**, 1, 81.

97. A.S. Singha and V.K. Thakur, *Bioresources*, 2009, **4**, 1, 292.

98. A.S. Singha and V.K. Thakur, *Iranian Polymer Journal*, 2008, **17**, 11, 861.

99. K. Bittler and W. Ostertagl, *Angewandte Chemie International Edition*, 1980, **19**, 190.

100. W. Feitknechti in *Pigments: An Introduction to their Physical Chemistry*, Elsevier, Amsterdam, The Netherlands, 1967.

4 Polymer Blends

4.1 Polymer Blends

Polymer blends are physical mixtures of structurally different polymers that adhere together. They adhere together through secondary bond forces, with no covalent bond between them [1]. The degree of crystallinity is one of the major factors determining the final properties of the blend by the size and distribution of segregated phases within the mixture. The main controlling factors include chemical composition, crystal structure and morphology, molecular weights (MW) and processing. Several important polymer pairs are compatible. However, most pairs exhibit pronounced incompatibility. Incompatibility leads to poor mechanical properties. The morphology depends on the arrangement of the phases, whether continuous or discontinuous, and crystalline or amorphous. The morphology of multiphase polymeric systems has a primary effect on blend properties [2–4].

Polymer blends offer the following attributes:

- They offer processors the most efficient way to satisfy new requirements for material properties.
- They fill economic and performance gaps.
- They provide improved processability.
- They are a relatively simple solution to a complex problem.

- They provide a reduction in costs
- They enable properties of importance to be maximised.
- They have interesting engineering applications.
- They are important for the preparation of materials with new desirable properties.

4.1.1 Morphology

Polymer blend morphology depends on the arrangement of the phases, continuous or discontinuous, and the degree of order in the crystalline or amorphous phases. The morphology of multiphase polymeric systems has a primary effect on their properties [4]. Single glass transition temperature (T_g) blends have interphase connections but are still not compatible.

Polymer blends may be divided into three categories:

- Those with crystalline interactions between two polymers;
- Those that have polymer interaction in the amorphous phase only; and
- Those that lack both crystalline and amorphous interactions but still have good mechanical properties.

In polymer blends where both polymers are crysallisable they can form mixed or separate crystals embedded in a compatible or incompatible amorphous phase. The crystals can be homogeneously dispersed or form various levels of superstructure. The structure of the blend will strongly affect its properties. Polymer blends of crystalline nature occupy only a small part due to their molecular incompatibility of the polymeric constituent with separate individual phases.

4.1.2 Physico-chemical Properties

The physico-chemical properties of polymer blends depend on several factors based on the polymer matrix present [5]:

- Adhesion in polymer blends;
- Concentration and distribution;
- Relaxation characteristics;
- Composition of the blend; and
- Temperature at which blending operation conducted.

4.1.3 Thermal Degradation

Thermal degradation in multiphase polymeric systems is a chemical process that generally takes place either through polymer molecules/long-chain radical species or through reaction involving small-molecule radical species that are produced in one phase and subsequently diffuse into other phase. The thermal degradation behaviour of polystyrene (PS) [6] and polypropylene (PP) [7, 8] can be profoundly influenced by the presence of a second polymer.

4.2 Immiscible Polymer Blends

Immiscible polymers exhibit inferior mechanical properties. This prevents their use in most commercial purposes. Immiscibility of polymers is a problem of poor stress transfer between component phases owing to a lack of adhesion or wetting. Additives such as compatibilisers might be expected to improve adhesion between the phases *via* an interfacial mechanism. The mechanical properties of immiscible blends should be very sensitive to the phase morphology generated during processing and also vary widely in chemical type. The chemical type of immiscible blends could be significantly improved by the addition of certain block copolymers. However, it is necessary to pay attention to the rheological characteristics and processing conditions. Otherwise, there is a possibility that heterogeneous structures would result in the blend. In ternary blends containing block copolymers, the formation of interlocking or interpenetrating network phases is the ideal morphology for an immiscible blend. This allows for equal sharing of imposed stresses by the components [9].

4.3 Commercial Blends

Many commercial plastics are in truth blends – a combination of two or more similar systems – such as linear and low-density polyethylene (LDPE), a formulation containing a number of incompatible polymers such as rubber-toughened materials like high-impact PS, or even a material that contains a 'polymeric plasticiser, such as poly(ethylene-*co*-vinyl acetate) in polyvinyl chloride (PVC) [10]. However, polymer blending constitutes much more than a mere technological expedient that enables compounding with improved materials to be devised by combining the useful properties of different molecular species in an effort to meet ever more demanding requirements. Indeed, the study of blends has done much to refine the fundamental understanding of polymeric materials and stimulate further research. Some of the concepts of blending two or more polymers together as a means of modifying macroscopic properties, as given below, have been widely adopted.

4.3.1 Polyolefin Blends

Polyolefin blends are of critical importance to the success of the material. Ethylene propylene diene rubber (EPDM) immiscibly blends with PP as an impact modifier. It is the most common and most commercially utilised blend of polyolefins. High-density polyethylene (HDPE) can be added to this blend to achieve maximum toughness [11–13]. Applications include wire and cable insulation, automotive bumpers and fascia, hose, gaskets, seals and weather stripping. These blends replace plasticised PVC and crosslinked rubbers where improved low-temperature flexibility, rubbery properties and thermoplastic characters are required.

HDPE immiscibly blends with butyl rubber [14] to provide improved chemical resistance, compression set and high-temperature mechanical properties *versus* unvulcanised blends. LDPE and HDPE blend immiscibly with ethylene copolymers to improve environmental stress crack resistance, toughness, filler acceptance, film tear resistance, improved flexibility and so on. In polyolefin, polybutene-1 forms miscible blends with PP [15, 16]. The addition of PP to polybutene-1 increases the crystallisation rate of polybutene-1 and would have utility as a nucleation additive.

4.3.2 Polystyrene Blends

PS has a low heat distortion temperature (HDT) and poly(2,6-dimethyl phenylene oxide) (PPO) has low processability. Blending PS with PPO leads to improved HDT and economy and processing characteristics [17–19]. Applications include appliance housings, automotive dashboards, pump components and television components. PS and polymethyl methacrylate (PMMA) form immiscible blends that exhibit a pearlescent appearance and are used for decorative applications [20].

4.3.3 Polyvinyl Chloride Blends

The most prominent application end-uses for PVC blends require permanent plasticisation. Butadiene/acrylonitrile copolymers have been compounded as permanent plasticisers for PVC wire and cable insulation, applications requiring food contact, and in pond liners used for oil containment [21]. Compounding with nitrile rubbers in plasticised PVC provides improved ozone, thermal ageing and chemical resistance for applications such as fuel hose covers, gaskets, conveyor belt covers and printing roll covers. The blend is miscible in the range of 23–45% acrylonitrile content in nitrile rubber [22]. In PVC blends, ethylene-vinyl acetate with a vinyl acetate content of 65–70 wt% serves as a permanent plasticiser [23]. However, it is amorphous and its gum stock type material presents a material handling problem.

PVC has a relatively low HDT. Several α-methylstyrene (α-mS)/acrylonitrile-*co*- and terpolymers improve the HDT on compounding with PVC [24–26]. Acrylonitrile-butadiene-styrene (ABS) blends miscibly [27] with PVC to improve flame resistance, and improves toughness and processability for applications in injection moulding, extrusion and thermoforming on compounding. Specific applications of ABS/PVC blends include interior truck panels, communication relays, electrical housings, appliance housings, mass transit interiors, and television housings [28]. In commercial blends, the acrylonitrile content of ABS is probably critical to miscibility and phase behaviour [29, 30].

PMMA/PVC blends provide heat resistance and chemical and flammability resistance into materials for injection moulding and extrusion applications. The major applications of these blends are interior panelling, trim and seat backs in mass transit vehicles. Commercially available PMMA is miscible with PVC [28, 31]. However, its phase behaviour is considered to be only partially miscible [29]. Chlorinated polyethylene blends with PVC have been used as impact modifiers and as secondary plasticisers [32]. Chlorine contents of 42% and 30% by weight lead to miscible and immiscible properties, respectively. Impact modification will generally require phase separation, and plasticisation will require miscibility.

Low-MW acrylics, styrene/acrylics and poly(α-methylstyrene) blend easily with PVC and improve processing, thermoformability, gloss and ductility [33]. Commercial PMMA systems have been found to be miscible with PVC [34]. Miscibility allows improved processability by breaking the structures of PVC particles.

4.3.4 Acrylonitrile-butadiene-styrene Blends

ABS with high heat resistance is based on the blending of α-mS/acrylonitrile and styrene/acrylonitrile copolymers at azeotropic compositions of 69:31 and 76:24 of (α-mS):acrylonitrile and styrene:acrylonitrile, respectively [35, 36]. ABS blends increase the HDT by 10–20 °C over that required for ABS. Application of these blends include short-term boiling water exposure, processing of parts requiring high-temperature finishing operations, and appliances such as washing machines, pans, and so on.

4.3.5 Polymethyl Methacrylate Blends

PMMA and polyvinylidene fluoride (PVDF) form miscible blends in which PMMA acts as a polymeric plasticiser when added in low amounts. PMMA improves processing and both PMMA and PVDF are resistant to ultraviolet degradation. Applications include weatherable film [37–41].

PMMA and polyethylene terephthalate (PET) as immiscible blends are commercially available. These blends are reinforced fibreglass, which is used in automotive and electrical markets, offering low warpage and fast moulding cycles [42]. PMMA and its copolymers with unsaturated polyesters develop as immiscible blends. These blends have been available commercially as low-profile additives for unsaturated polyester composites [43]. Shrinkage is controlled with this type of low-profile additive in polyester systems during the thermosetting step, thus yielding improved surface smoothness.

4.3.6 Polyester Blends

PET is a modifier that blends with polybutylene terephthalate (PBT) with miscible phase behaviour. It is commercially available for ready use. This blend exhibits improved surface gloss when compared to PBT alone. PET/PBT films have been suggested as a pressure-resistive adhesive-tape support [43, 44–47]. Poly(ε-caprolactone) (PCL) blends immiscibly with unsaturated polyesters and polyethylene (PE). PCL is used as low-profile additive for unsaturated polyesters [43], improving the surface and imparting better toughness. Polycarbonate (PC)/PE has the benefit of high energy absorption at low temperatures as its key property [48].

4.3.7 Polyamide Blends

Polyamide (PA)/maleic-anhydride (MA)-functionalised polyolefin (PO) blends provide a compatibility strategy consisting of maleation of the PO phase followed by a reactive processing favouring copolymer formation by imidisation between the anhydride and amine chain ends. The PO is most often ethylene-propylene copolymer rubber, PP or PE, and the PA is commonly PA6 or PA6,6 [49–58].

In PP-*g*-MA, MA grafting occurs onto PP chain ends after β scission. The anhydride grafted structure can be either single succinic-type anhydride or low-molecular-mass poly-MA [59]. Anhydride functions lie at the chain ends and the number-average MW decreases when the grafted anhydride concentration increases.

4.3.8 Polycarbonate Blends

PC offers toughness and heat resistance. ABS offers environmental stress-crack resistance and lower cost. Applications include automotive interior trim, business machines and electrical housings, and recreational vehicle and mass transit uses. ABS and polysulfone blends provide improved thermal and toughness properties along with electroplated parts requiring high temperature. Bisphenol A PC/ABS is an engineering polymer blend that is also used in electronic engineering, in transportation and in construction. PC/ABS blends are important industrial materials with good ductility, even after ageing. One of the strongest effects of the toughening of polymers is the change in the brittle–ductile transition

[60]. PCL is miscible with PC [61] as it is one of many possible aliphatic polyesters. Miscibility in polymer/polymer blends is the result of an exothermic heat of mixing caused by some specific interaction between polar groups within the two polymers [62].

4.4 Waste Plastic Blends

Among the various polymer blends and combinations, waste plastic utilisation seems to be of great value in a range of diverse applications. It is more versatile in applications such as building materials in coastal regions where corrosion is a main problem. Blends of PE and PP are used commercially because of their high impact strength and low-temperature toughness. Polyolefin is a major constituent of polymeric waste and scrap, and recycling is of considerable value.

Polymer blending techniques have been used to combine the best characteristics of each polymer. This improves the performance of polymeric materials, but it is necessary to combine the polymer blends in a relatively economic way [63, 64].

A mixture of a polymer with chemicals or other plastics is called blend. The basis for creating polymer blends is to exploit certain unique properties of individual polymers in multicomponent systems to the benefit of the overall properties. Polymer blends are gaining greater importance due to their unique properties, which differ from those of the basic polymers. Blending of one polymer with another polymer is a very common practice [65–70].

The selection of a suitable blend can be drawn from knowledge of the mechanical behaviour of the different polymers, as these will contribute to the design and quantitative scientific basis [71–75]. With the preparation of polymer blends, the synthesis of new polymers can be avoided. It is a comparatively cheap method, and another field of special interest. The creation of blends of waste or recycled plastics is very comparable to the synthesis of a polymer, with the different properties of waste plastics blended to create a new polymer.

The mechanical compatibilisation of polymer blends is conceptually an attractive route, leading to unique property combinations and the recycling of mixed polymer scrap. There is considerable impetus behind discovering polymers that exhibit such compatibilising effects and to understand the mechanisms by which they function. Blends would result if certain types of plastic soft-drink bottles were granulated and processed. A bottle type of interest consists of a PET container with an HDPE pedestal, which is needed because the blown bottle has a rounded bottom. It is quite obvious that PET and any PO would be grossly incompatible and that a very effective compatibiliser would be needed to give the blend adequate mechanical properties for any subsequent application [76].

4.5 Summary

- There are two types of polymer blends: miscible and immiscible.
- Miscible blends provide good mechanical and other physical properties.
- Immiscible blends, due to phase separation, have poor mechanical properties.
- Immiscible blends require suitable coupling agents as an additive.
- Blends are environmentally acceptable to minimise the requirement for natural resources.

References

1. J.A. Manson and L.H. Sperling in *Polymer Blends and Composites*, Plenum Press, New York, NY, USA, 1976, p.378.

2. S. Krause, *Journal of Macromolecular Science, Reviews in Macromolecular Chemistry and Physics*, 1972, **7**, 251.

3. M.B. Bever and M. Shen, *Materials Science and Engineering*, 1974, **15**, 145.

4. L.E. Nielsen in *Mechanical Properties of Polymers and Composites*, Marcel Dekker, New York, NY, USA, 1974, p.121.

5. C.B. Bucknall in *Toughened Plastics*, Applied Science Publishers, London, UK, 1977, p.173.

6. D.H. Richards and D.A. Salter, *Polymer*, 1967, **8**, 127.

7. Y. Mizutansi, S. Matsuoka and K. Yamamota, *Bulletin of the Chemical Society of Japan*, 1965, **38**, 2045 and 1966, **39**, 1792.

8. Y. Mizutansi, S. Matsuoka, K. Yamamota and S. Hisano, *Bulletin of the Chemical Society of Japan*, 1967, **40**, 1526.

9. D.R. Paul in *Polymer Blends*, Volume 11, Eds., DR. Paul and S. Newman, Academic, New York, NY, USA, 1978, Chapter 1.

10. D.R. Paul and S. Newman in *Polymer Blends*, Volumes 1 and 2, Academic Press, New York, NY, USA, 1978, pp.243–293 (Volume 1) and pp.35–89 (Volume 2).

11. L. D'Orazio, R. Greco, C. Mancarella, E. Martuscelli, G. Ragosta and C. Silvestre, *Polymer Engineering & Science*, 1982, **22**, 536.

12. H.L. Morris, *Journal of Elastomers and Plastics*, 1974, **6**, 121.

13. W.K. Fischer, *Modern Plastics*, 1974, **51**, 116.

14. A.Y. Coran and R. Patel, *Rubber Chemistry and Technology*, 1982, **53**, 141.

15. A. Piloz, J.Y. Decroix and J.F. May, *Angewandte Makromolekulare Chemie*, 1976, **54**, 77.

16. A. Siegmann, *Journal of Applied Polymer Science*, 1982, **27**, 1053.

17. W.J. Macknight, J. Stoelting and F.E. Karasz, *Advances in Chemistry Series*, 1971, **99**, 29.

18. A.R. Shultz and B.M. Gendron, *Journal of Applied Polymer Science*, 1972, **16**, 461.

19. A.R. Shultz and B.M. Beach, *Macromolecules*, 1974, **7**, 902.

20. O. Olabisi, L.M. Robeson and M.T. Shaw in *Polymer: Polymer Miscibility*, Academic Press, New York, NY, USA, 1979, p.245.

21. R.A. Emmett, *Industrial and Engineering Chemistry*, 1944, **36**, 730; and J.E. Pittenger and G.F. Cohan, *Modern Plastics*, 1947, **25**, 81.

22. G.A. Zakrzewski, *Polymer*, 1973, **14**, 348,

23. C.F. Hammer, *Macromolecules*, 1971, **4**, 69.

24. Y.C. Lee and G.A. Trementozzi, inventors; Monsanto Co., assignee; US 3644577, 1972.

25. K. Sugimoto, S. Tanaka and H. Fujita, inventors; Japanese Geon Co Ltd, assignee; US 3520953, 1970.

26. L. Scarso, E. Cerri and G. Pezzin, inventors; Montecatini Edison SpA, assignee; US 3772409, 1973.

27. Y.J. Shur and B.G. Ranby, *Journal of Applied Polymer Science*, 1976, **20**, 3121.

28. G.R. Forger, *Materials Engineering*, 1977, **85**, 44.

29. S. Krause, *Journal of Macromolecular Science – Reviews in Macromolecular Chemistry & Physics*, 1972, **7**, 251.

30. M.T. Shaw, *Polymer Engineering & Science*, 1982, **22**, 115.

31. D.J. Walsh and J.G. McKeown, *Polymer*, 1980, **21**, 1330

32. C.F. Hammer in *Polymer Blends*, Volume 2, Eds., D.R. Paul and S. Newman, Academic Press, New York, NY, USA, 1978, p.219.

33. J.T. Lutz, Jr, *Plastics Compounding*, 1981, Jan/Feb, 34.

34. J. Zelinger, E. Volfova, A.H. Zahradnikova and Z. Pelzbauer, *International Journal of Polymeric Materials and Polymeric Biomaterials*, 1976, **5**, 99.

35. H.H. Irvin, inventor; Borg Warner Corp., assignee; US 3010936, 1961.

36. R.J. Slocomb, *Journal of Polymer Science*, 1957, **26**, 9.

37. T. Nishi and T.T. Wang, *Macromolecules*, 1975, **5**, 909.

38. D.R. Paul and J.O. Altamirano, *Advances in Chemistry Series*, 1975, **142**, 354.

39. J.S. Noland, N.N.C. Hsu, R. Saxon and J.M. Schmitt, *Advances in Chemistry Series*, 1971, **99**, 15.

40. C.H. Miller, Jr., inventor; American Cyanamid Co., assignee; US 3458391, 1969.

41. F.F. Koblitz, R.G. Petrella, A.A. Dubert and A. Christofas, assignee; Pennwalt Chemicals Corp., assignee; US 3253060, 1966.

42. A.S. Wood, *Modern Plastics*, 1979, **56**, 44.

43. K.E. Atkins in *Polymer Blends*, Eds., D.R. Paul and S. Newman, Academic Press, New York, NY, USA, 1978, Chapter 23.

44. H.M. Li and A.H. Wong in *Polymer Compatibility and Incompatibility: Principles and Practices*, Ed., K. Solc, Harwood Academic Publishers, New York, NY, USA, 1982, p.373.

45. A. Escala, E. Balizer and R.S. Stein, *Polymer Preprints*, Division of Polymer Chemistry, American Chemical Society, 1978, **19**, 152.

46. J.S. Gall, inventor; Celanese Corp., assignee; US 4008199, 1977.

47. A.H. Wong, inventor; Minnesota Mining and Mfg Co., assignee; German Offen 2912610, 1979.

48. D.R. Paul and J.W. Barlow, *Journal of Macromolecular Science – Reviews in Macromolecular Chemistry & Physics*, 1980, **C18**, 1, 109.

49. F. Ide and A. Hasegawa, *Journal of Applied Polymer Science*, 1974, **18**, 963.

50. Y. Takeda, H. Heskkula and D.R. Paul, *Polymer*, 1992, **33**, 3173.

51. D. Brown and U. Elsenlohr, *Kunststoffe*, 1975, **65**, 139.

52. J. Rosch and R. Mulhaupt, *Macromolecular Rapid Communications*, 1993, **14**, 503.

53. Z. Liang and H.L. Williams, *Journal of Applied Polymer Science*, 1992, **44**, 699.

54. H.K. Chuang and C.D. Han, *Journal of Applied Polymer Science*, 1985, **30**, 165.

55. B.N. Epstein, inventor; E.I. Du Pont De Nemours and Co., assignee; US 4174358, 1979.

56. S.Y. Hobbs, R.C. Bopp and V.H. Watkins, *Polymer Engineering & Science*, 1983, **23**, 380; and G. Serpe, J. Jarrin and F. Dawans, *Polymer International*, 1990, **30**, 9, 553.

57. S. Schlag, J. Rŏsch and C. Friedrich, *Polymer Bulletin*, 1993, **30**, 603.

58. L.A. Utracki and P. Sammut, *Polymer Networks & Blends*, 1992, **2**, 23.

59. B. De Roover, M. Sclavons, V. Carlier, J. Devaux, R. Legras and A. Momtaz, *Journal of Polymer Science, Part A: Polymer Chemistry Edition*, 1995, **33**, 5, 829.

60. J.P.F. Inberg and R.J. Gaymans, *Polymer*, 2002, **43**, 3767.

61. C.A. Cruz, D.R. Paul and J.W. Barlow, *Journal of Applied Polymer Science*, 1979, **23**, 589.

62. D.R. Paul, J.W. Barlow, R.E. Bernstein and D.C. Wahrmund, *Polymer Engineering & Science*, 1978, **18**, 1225.

63. L.A. Utracky in *Commercial Polymer Blends*, Chapman & Hall, London, UK, 1998, p.117.

64. I. Vinckier, P. Moldenaers and J. Mewis, *Journal of Rheology*, 1996, **40**, 613.

65. J.A. Manson and L.H. Sperling in *Polymer Blends and Composites*, Plenum Press, New York, NY, USA, 1976, p.373.

66. S. Kreuse in *Polymer Blends*, Eds., D.R. Paul and S. Newman, Academic Press, New York, NY, USA, 1978, Chapter 2.

67. A.Y. Coran, B. Das and R.P. Patel, inventors; Monsanto Co., assignee; US 4130535, 1978.

68. A.K. Sen, B. Mukherjee, A.S. Battacharyya, P.P. De and A.K. Bhowmick, *Polymer Degradation and Stability*, 1992, **281**, 36.

69. W. Michaeli, M. Cremer and R. Bluhm, *German Plastics*, 1993, **83**, 992.

70. W. Wenig and M. Asresahegn, *Polymer Engineering & Science*, 1993, **3**, 877.

71. W. Weing and A. Waslak, *Colloid and Polymer Science*, 1993, **273**, 824.

72. B.K. Kim, M.S. Kim and K.J. Kim, *Journal of Applied Polymer Science*, 1993, **48**, 1271.

73. C.L. Wang, S.J. Wang, W.G. Zheng and Z.N. Qi, *Journal de Physique*, 1993, **3**, 261.

74. Y. Kim, C.S. Ha, T. Kang and W.J. Cho, *Journal of Applied Polymer Science*, 1994, **51**, 1453.

75. C.S. Ha, Y. Kim and W.J. Cho, *Journal of Applied Polymer Science*, 1994, **51**, 1381.

76. A. Rudin, D.A. Loucks and J.M. Goldwasser, *Polymer Engineering & Science*, 1980, **20**, 741.

5 Polymer Composites

Polymer modification can follow from the mixing of two or more macromolecular compounds or their filling with reinforcing materials of inorganic or organic substances. It enables the production of composites with required properties. Introducing reinforcing material changes the kinetics and thermodynamics of polymer crystallisation. Therefore, the importance of composite materials is increasing with the demand for high performance and low operational costs.

Some reinforcing materials in polymer composites are inexpensive, so the output in manufacture is higher per employed material if fillers or blends are used. By mixing, filler or second polymers can be incorporated into a given polymer. However, the homogeneity of the composite is often an unsolved problem. If a polymer composite is to be manufactured as a mixture of polymers, the first polymers are generally the seeds for polymerisation reactions of the second polymer. Miscibility is limited by the entropy effects of the systems, which are usually heterogeneous. Phase separation is minimised by, for example, crosslinking one polymer.

5.1 Essentials of Polymer Composites

Polymer composites are widely used in science and industry due to their light weight and many tailored properties. Polymeric materials have a wider range of properties than pure polymers, which has an economic influence. The main polymer parameters, including molecular weight (MW), crystallinity, characteristics of the reinforcing material, the effect of the interface on the properties, are involved in composite manufacturing. These can be obtained by an appropriate choice of components and suitable processing conditions.

Thermoset materials are produced by the direct formation of network polymers from monomers, or by crosslinking linear prepolymers. Important thermosets include alkyds, amino and phenolic resins, epoxies, unsaturated polyesters and polyurethanes. Thermosetting polymers consist of two liquid components, one containing a resin and the other a hardener [1].

In composites, particulate inorganic fillers or reinforcing materials such as fibres are commonly added to thermoplastic and thermoset polymeric materials to achieve economy while modifying certain properties such as stiffness, heat distortion and mouldability. However, there are certain properties such as toughness and ultimate elongation that usually deteriorate.

Polymer composites are widely used to replace traditional materials such as metal in applications that require high strength and stiffness in combination with low weight. The majority of polymer composites are based on glass or carbon fibre combined with thermoset polymeric materials as the polymer matrix material. Thermoplastic polymeric materials have the natural advantage of being recyclable, among other beneficial properties. However, poor fibre impregnation and wetting characteristics have limited the use of thermoplastic composites.

Fibre-reinforced polymer composites (FRP) are lightweight and very durable, but their initial cost is higher than that of steel. However, these materials compare well on the basis of their lower construction and long-term maintenance costs. FRP have not realised their potential in construction applications. Contributing factors include the perceived expense and a lack of confidence on the part of clients and designers.

The term FRP describes a group of materials composed of organic or inorganic fibres embedded in a polymer matrix. Material with high strength and stiffness is required in many construction applications. The most commonly used reinforcing fibres are glass, aramid and carbon. In FRP, the matrix materials have primarily been thermoset resins such as polyesters, epoxies and vinylesters. FRP are elastic and do not yield [2]. The use of conventional thermoplastic materials such as polypropylene (PP) and Nylon in composites is distinctly different from using thermosets.

Given that the recycling possibilities of thermoplastic matrices are attractive, bottles made from thermoplastic-based systems could potentially be reused. The properties of glass fibre/recycled polyethylene (PE) terephthalate suggest that recycled thermoplastics have significant potential as matrix materials [3]. Similarly, the use of recycled acrylonitrile-butadiene-styrene from shredder residue from computer and monitor housings has significant potential [4]. Sustainability issues are becoming increasingly important, so the recycling possibilities of thermoplastic matrices are expected to be attractive. Domestic waste systems contain vast amounts of thermoplastic-based bottles and could potentially be reused [3].

5.2 Thermoplastic Polymeric Composites

Thermoplastic polymeric composites are manufactured by dispersing reinforcing materials or fillers into molten plastics to form composite materials *via* processing techniques such as extrusion, thermoforming and compression moulding [5, 6]. The majority of polymers are immiscible, so, to improve adhesion between the phases, some effects occurring at the phase boundary are of great importance. With any system of two polymers there is the possibility of a mutual influence of the reinforcing material on the polymer matrix and *vice versa* [7–11].

5.3 Thermoset Polymeric Composites

Thermoset polymeric composites are produced by impregnating reinforcing material or filler with monomers and initiators or prepolymers [12, 13]. Polymer formation can be initiated by a chemical catalyst, gamma radiation or heat reaction to form a high-MW polymer and composites [14–17]. Thermosetting composites require the processing of base materials with a careful application of compounding and processing conditions in order to control the development of viscosity. Viscosity is dependent on the temperature and on the polymer structure. Continuous changes in the resin – from a low-viscosity liquid monomer at the compounding point to a solid polymer at the end of the process – affect the fibre wettability, the formation and growth of bubble, and composite consolidation.

Control of the processing of compounded materials on scientific bases requires accurate knowledge of the polymerisation kinetics of the matrix as a function of the applied processing temperature. Optimisation and control are based on the curing kinetics and fundamental transport phenomena associated with the specific processing technology, with selection of appropriate temperatures and pressures to be applied during curing of the matrix composites [18, 19].

5.3.1 Fibre-reinforced Composites

Fibre-reinforced composites offer a combination of properties not found in other materials, such as high strength and dimensional stability, combined with low weight, corrosion and chemical resistance and excellent dielectric properties [20, 21]. These composites are as strong as conventional materials and more resilient, and absorb shock to a degree rather than transmitting it.

5.3.1.1 Curing

The curing of thermoset polymeric materials can be represented in terms of a time/temperature/transformation cure diagram, as schematically represented in **Figure 5.1**. In the cure diagram the times to gelations, induction time, maximum polymerisation degree and vitrification are plotted versus cure temperature [22, 23].

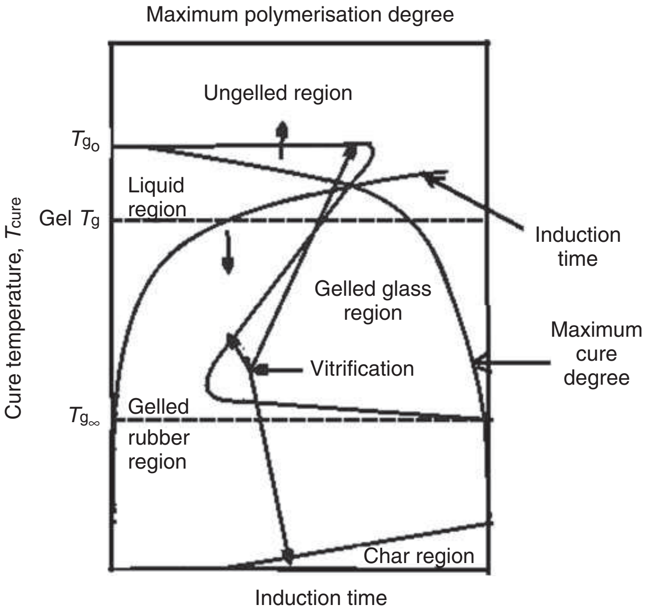


Figure 5.1 Schematic representation of an induction time *versus* cure diagram

In the figure, the S-shaped vitrification curve and the gelation divide the time/temperature plot into four distinct states – liquid, gelled rubber, ungelled glass and gelled glass – along with induction time and maximum cure degree. T_{g0} is the glass transition temperature of the unreacted resin mixture, $T_{g\infty}$ is the glass transition temperature of the fully cured resin, and gel T_g is the glass transition temperature of the resin at its gel point. At a cure temperature sufficiently below $T_{g\infty}$ the reaction will not go to completion due to the viscosity increase as a result of increasing MW. The reaction becomes diffusion-controlled and is eventually quenched as the material vitrifies [24]. The reaction increases as the cure temperature is raised, attains the full extent of conversion, and ends with quenching. An increase in the glass transition temperature and other parameter changes that occur during curing can be monitored as a function of the extent of cure [25, 26].

Polymer composites have a fracture toughness, ultimate tensile strength and ultimate elongation that can be varied by changing the glass transition temperature of the composite. The thermodynamic properties of the amorphous matrix change at T_g.

In summary:

- The polymer must wet the surfaces of the reinforcing material during mixing, promoting continuous phase boundaries.
- A significant fraction of the polymer must be in contact with the reinforcing material.
- The degree of interaction must be demonstrated by changes in the thermodynamic and viscoelastic properties of the matrix.
- The strength across the phase boundaries, or adhesion, will naturally have effects on the stress–strain behaviour.

5.4 Applications

Inorganic fillers are widely used to reinforce polymers to improve their properties. Organic fibres such as cellulose-based fibres have started to replace synthetic minerals [27–35]. The main disadvantage of organic fibre is its enhanced moisture absorption and the poor adhesion between hydrophilic fibres and the hydrophobic polymer matrix.

5.5 Polyolefin Composites

The toughness of composite materials filled with rigid inorganic particles will be improved or enhanced to different extents with the use of plastics. Glass beads are used in industry because of their strong filling ability, smooth spherical surfaces, small and well distributed internal stress in the products and good processibility of the filled materials. Viscoelastic behaviour such as die-swell, melt fracture and wall slip of glass bead-filled high-density polyethylene (HDPE) composite [36] and the rheological and mechanical properties of glass bead-filled PP composites [37] indicates that these properties are based on bead fractions and filler concentrations. Also, the relative tensile modulus and relative flexural modulus are both linear functions of bead fraction and filler concentration.

Even PE, PP and polyvinyl chloride resins, still the most commonly used thermoplastic polymeric materials with wood, have low thermal stability above 200 °C. However, their inherently undesirable mechanical properties, such as the creep-resistant properties of the polyolefin matrix, have impeded further applications of the wood plastic composites (WPC) as structural composite materials. In attempts to overcome these drawbacks, attention has been given to the silane-crosslinking of wood/PE composites [38], the use of high-performance engineering thermoplastics such as Nylon 6 [39] as a single polymeric matrix, the modification of the matrix by incorporation of organoclay [40], and stretching wood/PP composites [41].

5.6 Highly Filled Elastomers

The mechanical properties of highly filled elastomers have led to their use as solid propellants in rocketry. Composite propellants consist of elastomers highly filled with inorganic oxidiser. Mixing is effected in an uncrosslinked state in which the polymer still has a low MW and the consistency of a viscous fluid. The compounded mixture is cast or extruded into the desired shape and hardened by polymerisation and crosslinking. The degree of loading for the systems is very high and depends on the composition [42].

5.7 Polyamide 6 Composites

Polyamide (PA) 6 composites show severe discoloration and pronounced pyrolytic degradation. With the high processing temperatures (>220 °C) for engineering thermoplastics, cellulose fibres undergo severe thermal degradation [43]. This thermal degradation can be reduced by using purified pulp fibres with a cellulose content greater than 80% and by adding the fibres into premelted polymer downstream of a twin screw extruder [43, 44].

5.8 Natural Fibre Composites

Worldwide ecological concern has resulted in an interest in renewable natural materials. Natural organic fibres are derived from renewable bioresources. They can act as biodegradable reinforcing materials and are an alternative to glass or carbon fibres and inorganic fillers [45].

Natural fibres are light, low in density, low in cost, renewable, recyclable, CO_2-neutral and biodegradable. It is generally believed that composites containing natural fibres are the future of structural materials [46]. However, wood fibre is still the most widely used material in composites [47]. With a view to achieving a sustainable development economy, it would be ideal to replace wood (which is valuable, useful for multiple applications, but expensive and time consuming to prepare as the wood raw material) with other types of agrowaste, such as wheat straw [48, 49], corn stalks and corncobs [48], bagasse, cotton stalk and banana plant waste, rice straw [50], sugar cane, apple and orange fruit juice extraction waste [51] as potential fillers. Indeed, in thermoplastic polymeric composites, natural fibres from agriculture have emerged as alternative fillers. The natural fibres are renewable and low-cost materials and combine with PP to provide engineering products with unique characteristics.

5.9 Wood Plastic Composites

WPC have successfully proven their application in various fields, including lumber, decking and railing, window profiles, wall studs, door frames, furniture, pallets, fencing, docks, siding, architectural profiles, boat hulls and automotive components. The market for WPC has been experiencing growth both in North America and Europe [52].

The advantages of WPC include increased bending strength, stiffness (flexural and tensile modulus), reduced thermal expansion and cost. Mechanical properties such as creep resistance, modulus and strength are usually lower than those of solid wood. WPC are not being used in applications that require considerable structural performance [53], although in early 1984, cellulose flour was used to reinforce PA to give PA 12 [54].

WPC take advantage of the properties of both wood and plastics. The advantages of wood include low density, low equipment abrasiveness, relatively low cost and good biodegradability. However, plastics provide WPC with good moisture and decay resistance [5, 55]. In addition, various surface optical effects can be obtained by adding different wood species and coloured pigments [56]. Thermoplastics commonly used for manufacturing WPC include HDPE, low-density PE [57, 58] and PP [59–61].

In spite of the advantages, the use of wood in thermoplastics has been plagued by the thermal stability limitation of wood, and the difficulties in obtaining good filler dispersion and strong interfacial adhesion [62, 63]. This is because of the natural incompatibility between the hydrophilic, polar wood fibres and the hydrophobic, nonpolar thermoplastics. Such phase incompatibility causes a weak interface between the wood filler and the matrix. Moreover, strong wood–wood interactions resulting from hydrogen bonding and physical entanglement impair the dispersion of such filler in the viscous matrix [64, 65].

5.10 Phenol-formaldehyde and Urea-formaldehyde

Thermoset composites are mainly considered due to their intrinsic fire resistance. They provide low flame spread and very low smoke emissions without any addition of halogenated fire retardants or higher loading of filler or reinforcing materials. Phenol-formaldehyde and urea-formaldehyde are the most common thermosetting resins used as adhesives for wood composite products, including plywood, particleboard, fibreboard and oriented strand board [66–69].

5.11 Shortcomings

The shortcomings experienced with fibre-reinforced composites show that the forming of straight, continuous fibre or woven fibre composite sheets typically results in wrinkling of the fibres and distortions.

Polymer composites are utilised to meet structural and non-structural functional requirements. They are used in high-volume applications such as automotive, trucking, agricultural equipment, rail cars, high-speed civil transportation, off-shore and in-shore marine, sporting goods, civil infrastructure and bridge rehabilitation. The fibre matrix interface, the polymer–polymer interface, plays a crucial role in the economic competitiveness of composite manufacturing.

The ability of polymer composites, especially thermoset polymers and their composites, to be repaired, recycled and bonded depends on the physical and chemical nature of the polymer surface combined with the manufacturing process. The interfaces can be numerous.

5.12 Summary

- Polymer composites are lightweight with enhanced physical properties.

- Natural fibres can be used as filler instead of mineral fillers.

- The miscibility of polymers is limited by the entropy effects of the systems.
- Composites utilise waste material, the benefits of which are of worldwide ecological concern.
- Polymer composites can replace metals in applications that require high strength and stiffness.

References

1. C. Hall in *Polymer Materials, Higher and Further Education Division*, Macmillan Publishers, London, UK, 1985.
2. K.A. Soudid, *Progress in Structural Engineering and Materials*, 1998, **1**, 2, 135.
3. W.J. Cantwell, *Journal of Reinforced Plastics and Composites*, 1999, **18**, 4, 373.
4. P.V. Vijay, H.V.S. Ganga Rao and J.M. Bargo in *Advanced Composite Materials in Bridge and Structures*, Eds., J.L. Humar and A.G. Razaqpur, The Canadian Society for Civil Engineering, Montreal, Quebec, Canada, 2000, **53**, 60.
5. C. Clemons, *Forest Products Journal*, 2002, **52**, 6, 10.
6. M. Ford in *Proceedings of the 5th International Conference on Woodfiber-Plastic Composites*, Forest Products Society, Madison, WI, USA, 1999, p.199.
7. C.E. Locke and D.R. Paul, *Journal of Applied Polymer Science*, 1974, **17**, 2597 and 2791.
8. W.M. Barentsen, D. Hrikens and P. Piet, *Polymer*, 1974, **15**, 119.

9. F. Ide and A. Hasegawa, *Journal of Applied Polymer Science*, 1974, **18**, 963.
10. E. Helfand and Z. Wassermann, *Polymer Engineering & Science*, 1977, **17**, 118.
11. R.L. Scott, *Journal of Chemical Physics*, 1949, **17**, 279.
12. M.H. Schnieder, *Wood and Fiber Science*, 1994, **26**, 142.
13. M.H. Schnieder, *Wood Science and Technology*, 1995, **29**, 121.
14. J.A. Meyer, *Forest Products Journal*, 1965, **15**, 362.
15. U.P. Wang, *Journal of the Chinese Chemical Society*, 1975, **22**, 77.
16. A. Hebeish and J.T. Guthrie in *Polymer/Properties and Applications*, Springer-Verlag, New York, NY, USA, 1981.
17. A.E. Witt, *Radiation Physics and Chemistry*, 1981, **18**, 67.
18. J.M. Kenny, A. Apicella and L. Nicolais, *Polymer Engineering & Science*, 1989, **29**, 973.
19. J.M. Kenny, A.M. Maffezzoli and L. Nicolais, *Composites Science and Technology*, 1990, **38**, 339.
20. J.G. Mohr, S.S. Oleesky, G.D. Shook and L.S. Meyer in *SPI Handbook of Technology and Engineering of Reinforced Plastics Composites*, 2nd Edition, Van Nostrand Reinhold, New York, NY, USA, 1973.
21. *Handbook of Fiberglass and Advanced Plastics Composites*, Ed., G. Lubin, Van Nostrand Reinhold, New York, NY, USA, 1969.

22. J.K. Gillham in *Developments in Polymer Characterization 3*, Ed., J.V. Dawkins, Applied Science, London, UK, 1982, p.159.

23. J.B. Enns and J.K. Gillham, *Journal of Applied Polymer Science*, 1983, **28**, 2831.

24. J.B. Enns and J.K. Gillham in *Computer Applications in Applied Polymer Science*, Ed., T. Provder, ACS Symposium Series No.197, American Chemical Society, Washington, DC, USA, 1982, p.329.

25. J.B. Enns and J.K. Gillham, *Journal of Applied Polymer Science*, 1983, **28**, 2567.

26. J.B. Enns and J.K. Gillham, *Journal of Applied Polymer Science*, 1983, **28**, 2831.

27. A.K. Bledzki and J. Gassan, *Progress in Polymer Science*, 1999, **24**, 221.

28. Y. Li, Y-W. Mai and L. Ye, *Composites Science and Technology*, 2000, **60**, 2037.

29. K. Joseph, S. Thomas and C. Pavirthran, *Polymer*, 1996, **37**, 5139.

30. C. Albano, J. Gonzalez, M. Ichazo and D. Kaiser, *Polymer Degradation and Stability*, 1999, **66**, 179.

31. J.M. Felix and P. Gatenholm, *Journal of Applied Polymer Science*, 1993, **50**, 699.

32. A. Amash and P. Zugenmaier, *Polymer Bulletin*, 1998, **40**, 251

33. K. Van de Velde and P. Kiekens, *Polymer Testing*, 2001, **20**, 885.

34. G.C. Stael, M.I.B. Tavares and J.R.M. d'Almeida, *Polymer Testing*, 2001, **20**, 869.

35. H.P.S.A. Khalil, H. Ismail, H.D. Rozman and M.N. Ahmad, *European Polymer Journal*, 2001, **37**, 1037.

36. T.T.S. Lim, *Polymer Engineering & Science*, 1977, **11**, 240.

37. D.I. Faulkner and L.R. Schmid, *Polymer Engineering & Science*, 1977, **17**, 9, 657.

38. M. Bengtsson, P. Gatenholm and K. Oksman, *Composites Science and Technology*, 2005, **65**, 10, 1468.

39. R. Jacobson, D. Caulfield, K. Sears and J. Underwood in *Proceedings of the 6th International Conference on Woodfiber-Plastic Composites*, Forest Products Society, Madison, WI, USA, 15–16th May, 2001, p.127.

40. Y. Zhong, T. Poloso, M. Hetzer and D.D. Kee, *Polymer Engineering & Science*, 2007, **47**, 6, 797.

41. R.W. Newson, P.G. Osbome and F.W. Maine in *Proceedings of the Progress in Woodfibre–Plastic Composites Conference*, 25–26th May, Toronto, Canada, 2000.

42. C.W. van der Wal, H.W. Bree and F.R. Schwarzl, *Journal of Applied Polymer Science*, 1965, **9**, 2143.

43. K.D. Sears, R. Jacobson, D.F. Caufield and J. Underwood in *Proceeding of the 6th International Conference on Wood Fiber–Plastic Composites*, Forest Products Society, Madison, WI, USA, 2001, p.181.

44. D.F. Caufield, R.E. Jacobson, K.D. Sears and J. Underwood in *Proceedings of the 2nd International Conference on Advanced Engineered Wood Composites*, 2001.

45. N. Saheb and J.P. Jog, *Advances in Polymer Technology*, 1999, **18**, 4, 351.

46. P. Wambua, J. Ivens and I. Verpoest, *Composites Science and Technology*, 2003, **63**, 1259.

47. A.K. Mohanty, M. Misra and I.T. Drzal in *Natural Fibres, Biopolymers, and Biocomposites*, CRC Press and Taylor & Francis Group, Boca Raton, FL, USA, 2005.

48. S. Panthapulakkal and M. Sain, *Composites Part A: Applied Science and Manufacturing*, 2007, **38**, 1445.

49. A. Alemdar and M. Sain, *Composites Science and Technology*, 2008, **68**, 557.

50. J. Habibi, W.K. EJ-Zawawy and M.M. Ibrahim, *Composites Science and Technology*, 2008, **68**, 1877.

51. E. Chiellini, P. Cinelli, S.H. Imam and L. Mao, *Biomacromolecules*, 2001, **2**, 1029.

52. A. Alireza, *Bioresource Technology*, 2008, **99**, 4661.

53. C. Clemons, *Forest Products Journal*, 2002, **25**, 6, 10.

54. C. Klason, J. Kubåt and H.E. Strömvall, *International Journal of Polymeric Materials and Polymeric Biomaterials*, 1984, **10**, 159.

55. W.G. Glasser, R. Taib, R.K. Jain and R. Kander, *Journal of Applied Polymer Science*, 1999, **73**, 1329.

56. A.K. Bledzki, S. Reihmane and J. Gassan, *Polymer–Plastics Technology and Engineering*, 1998, **37**, 451.

57. R.G. Raj, B.V. Kokta, G. Groleau and C. Daneault, *Plastics, Rubber and Composites Processing and Applications*, 1989, **11**, 215.

58. K. Oksman and H. Lindberg, *Journal of Applied Polymer Science*, 1998, **68**, 1845.

59. M. Kazayawoko, J.J. Balatinecz, R.T. Woodhams and S. Law, *International Journal of Polymeric Materials and Polymeric Biomaterials*, 1997, **37**, 237.

60. H. Kishi, M. Yoshioka, A. Yamanoi and N. Shiraishi, *Journal of Wood Science*, 1988, **34**, 133.

61. G.E. Myers, I.S. Chahyadi, C.A. Coberly and D.S. Ermer, *International Journal of Polymeric Materials and Polymeric Biomaterials*, 1991, **15**, 21.

62. B.V. Kokta, D.P. Kamdem, A.D. Beshay and C. Daneault, *Polymer Composites*, 1986, **7**, 251.

63. A.K. Bledzki, J. Gassan and S. Theis, *Mechanics of Composite Materials*, 1998, **34**, 563.

64. M. Kazayawoko, J.J. Balatinecz and L.M. Matuana, *Journal of Materials Science*, 1999, **34**, 6189.

65. J.Z. Lu, Q. Wu, and H.S. McNabb, Jr., *Wood and Fiber Science*, 2000, **32**, 88.

66. D.P. Kamdem and B. Riedl, *Colloid and Polymer Science*, 1991, **269**, 595.

67. D.P. Kamdem and T. Sean, *Forest Products Journal*, 1994, **44**, 2, 65.

68. S. Hiziroglu and D.P. Kamdem, *Forest Products Journal*, 1995, **45**, 11/12, 66.

69. J.M. Muson and D.P. Kamdem, *Forest Products Journal*, 1998, **48**, 3, 55.

6 Polymer Compounding – Requirements

Polymers are long-chain molecules with unique properties, and different chemical structures and morphologies. Polymers are finding widespread use due to their economic and social importance and the wide range of emerging products in chemistry, engineering, medicine and biotechnology. Accordingly, polymer compounding has received a great deal of attention because of its fundamental scientific interest and potential utility.

Compounding is a complex processing method for obtaining materials with expected properties (including melt flow index, oxidation induction time and mechanical properties) during processing.

6.1 Fundamentals of Compounding

Compounding requires knowledge of the capabilities and weaknesses of individual polymers in order to improve the properties that will be required of them during their use. It acts to improve the performance of a polymer in the application for which it is to be used.

- It is used to formulate a compound that will process satisfactorily in the available equipment.
- It facilitates the required service or performance of the material.
- It helps to improve the use of end products in applications through the addition of additives during compounding.

Compounding provides a material that:

- Is free from contamination;
- Is stabilised even after compounding; and
- Has an even and consistent distribution of additives to improve end-product properties.

6.2 Essentials of Compounding

In compounding, it is essential to know about:

- Ingredients;
- Formulation;
- Morphology;
- Polymer melt;
- Processing requirements; and
- Temperature.

6.2.1 Ingredients

Polymers are combined with additives to enhance their processing and economy. Before beginning compounding, it is essential to have as much information as possible about all the ingredients, including:

- The properties and other information about the ingredients and polymer;
- Their rheological and thermodynamic behaviour;

- Their density, for the behaviour of the process;
- The composition of the compound; and
- The homogeneity of the compound.

6.2.2 Formulation

A basic formulation requires there to be a majority of polymer with additives provided as minor ingredients. By manipulating a basic range of additives, the physical properties of the compound can be improved. The type and level of addition of additives should be based on the degree of performance contributed per unit of addition, with an optimum level required to give maximum performance, even under the most adverse conditions, while considering the cost of achieving these performance levels.

6.2.3 Morphology

Morphology can affect many physical and mechanical properties, including impact strength, elongation strength and permeability characteristics [1–3]. While compounding, complicated morphologies are formed and can be controlled [4–6]. With polymer–polymer blends, the co-continuity and phase inversion after compounding maintain their continuity.

6.2.4 Polymer Melt

The polymer melt is one of the important factors determining the usefulness of a material and its ease of processing while compounding. The material process depends entirely on the condition of the polymer and the ingredients to be added. During compounding, however, molten polymer is normally exposed to high temperatures, shear and the presence of oxygen and impurities like hydro-peroxides and catalyst residues before undergoing processing. This can cause changes in the molar mass distribution. However, uniformity in the compound helps in processing the material through the processing equipment. Many different chemical agents are added to polymers during compounding, and in some processes chemical reactions occur, as in the production of polymeric foams or thermoset resins.

6.2.5 Processing Requirements

Compounding is a multicomponent polymer system. The distribution or response of the ingredients present in the compound may differ for each component. The proper choice of additive and the selection of processing conditions after compounding are more critical than for a single polymer.

In compounding, miscible and partly miscible additives are used in low concentrations. These additives may include various compatibilisers, crosslinking agents and stabilisers to heat, light and so on. The degree of polymer compounding is controlled by:

- Chemical structure;
- Molecular weight (MW);
- Concentration of additives at the processing temperatures;
- Type of additive;
- Requirement of performance characteristics;
- Type and magnitude of interactions with the polymer;
- Solubility parameters; and
- Solubility and diffusivity during heating while compounding.

In addition to this, it is necessary to note the composition of the melt in terms of:

- Mass contents;
- Volume contents; and
- Starting components.

6.2.6 Temperature

Compounding ingredients are rarely defined chemically unless they are well-known chemicals first produced from other sources. In compounding, as a rule, it is necessary to know the chemical composition of the other materials. Temperature is one of the most important parameters the compounding and polymer processing. The temperature can significantly change the rheology of polymers and aspects such as the solid, crystal or liquid state of the different additives.

6.3 Melt Compounding

The melt compounding process comprises an energy balance on the particle surface. In the first phase, particles are in powder form, and the polymer melt mixed with the additives is seen as a continuum. The heat flow distribution by the melt, through transient heat conduction, leads to an increase in the temperature of the solid particles for a specific period of time. The heat flow can therefore occur on the melt side if the radial temperature around a polymer is known. The polymer to be melted is embedded in the melt in the completely filled melting zone. The additives and fillers are directly wetted by the melt and are incorporated.

The point at which melting commences is taken as the point of the first complete screw filling. At the commencement of the melting process, the differential axial conveying velocities in the melting area and in the solids conveying zone give a mixture of melt in which solid particles are dispersed unevenly.

In compounding, the development of the melt temperature is heavily linked to melting of the solid material in the screw channel. The temperature around the material is important for the melting process. In particle/fluid systems, the shear rate increases due to the flow cross-section of the liquid being reduced by the presence of the solid material.

The aim of mixing in compounding is to homogenise the components. This means the distribution of melt particles within a given volume, where the melt particles differ in at least one property [7, 8]. When compounding in an extruder, there is distributive and dispersive mixing. Distributive mixing evenly distributes the mixing components, while dispersive mixing reduces the size of agglomerates and then disperses the fragments in the melt. Dispersing of material is the general trend of the two mixing processes.

6.3.1 Masterbatch

The use of a masterbatch features widely in compounding and with different polymer materials. A masterbatch usually incorporates a high loading of up to 60% by weight of one or more additive ingredients dispersed in a carrier polymer. The uniformity of the finished product is largely dependent upon the degree of dispersion of the masterbatch in the main polymer during melt processing. However, the performance of the masterbatch depends on the relative magnitude of its viscosity compared to that of the host polymer. Other parameters such as particle size and miscibility of the ingredients also play an important role.

6.4 Blender Mixing

6.4.1 Compounding of Rigid Polyvinyl Chloride

A high-intensity blender with propeller-type blades is used, which rotates at very high speed and causes a vortex mixing action. It provides uniform mixing of all the compounds. The direct benefit of compounding by dry blending is obtaining free-flowing blends that are free of agglomerates. Resin particles are uniformly coated with stabiliser, lubricant and filler. It therefore ensures homogeneous chemical and physical properties of the moulding or extrudates.

All the ingredients are added except for the filler, and the blender is allowed to operate until the temperature reaches about 80 °C. It is stopped to add filler, and then put to work until the temperature of the blend reaches about 110–120 °C. It is then emptied and cooled. The addition of liquid stabilisers at a higher temperature may cause the stabilisers to vaporise due to the heat. Higher-output extrudates are obtained within a temperature range of 105–125 °C. Much higher speeds cause slower rates of extrusion due to the greater compactness of the particles [9].

When a polymer in powder form is placed in an internal mixer and the temperature is raised by the shearing action of the equipment, this acts upon the particulate mass; the reaction of the mass is dependent upon its frictional properties, that is, its external friction (powder to metal) and its internal friction (powder to powder). As the temperature of the environment increases, the crystallites start to melt and molecular chain mobility increases. The effects of shear on the supermolecular chain mobility increase the effects of shear on the molecular structure, and begin to destroy the particle boundaries. As shearing increases, a change in diffusion occurs across the old boundaries as well as entanglement of the polymer during heating. Polymer chain involvement from one domain to another occurs up to degradation temperatures. This is transported at the molecular level as greater fusion and therefore increasing molecular mobility, and hence entanglement as cooling crystallites are reformed from convenient chain segments, resulting in a newly formed network being locked into place. The degree of fusion is thus the degree to which the network is formed. The fusion is the progressive breakdown of the particulate structure with the parallel development of a molecular network.

6.5 Devolatilisation

In many compounding operations it is necessary to remove volatile components from melts or solution in order to avoid voids and sinks, thereby improving product quality, reducing waste, improving economy and eliminating health hazards. Devolatilisation is one of the important operations in the compounding and processing of polymers.

In polymers, volatile species can be residual monomers, reaction by-products or solvents. Devolatilisation extracts volatile vapours by the application of reduced pressure or vacuum. It often involves the injection of a stripping agent during compounding to enhance the devolatilisation performance. Water and nitrogen are two commonly used stripping agents. As a result of devolatilisation, bubbles of the volatile components and stripping agent are generated [10]. The particular aspects of polymer devolatilisation applied depend upon the polymer and the ingredients used in compounding. Major operations use vacuum to eliminate the volatile species during the compounding process [11].

The vacuum section for devolatilisation usually starts at some distance after the polymer melt seal. The melt seal is formed by passing the polymer through a high-pressure zone, for example by pressure build-up through the reverse pitch screw elements in a co-rotating twin-screw extruder. Large-pitch forward-conveying screw elements are used in the vacuum section, resulting in partially filled screw channels to accommodate foaming.

6.6 Importance of Compounding

Compounding is an important operation which helps in:

- The processing of material;
- Production requirements such as throughput, modulation in temperature, devolatilisation efficiency and improved design factor;
- The design of the initial screw configuration and other process parameters; and
- Machine operating conditions.

It is essential to monitor the extent of mixing during a compounding process as poor compounding may lead to:

- Product failure because of regions of insufficient compounding, which could act as points of weakness;
- A requirement for extra processing time in order to achieve sufficient mixing during processing, which may require more energy input and lead to a reduction in production capacity; and
- A requirement for more additives or pigment to be used in order to ensure that minimum quality is maintained to make up for insufficient compounding.

6.7 Optimisation

Polymer compounding in most cases not only influences the properties of the end product but also has a considerable effect on the processing conditions. Compounding is used not only to produce changes in thermodynamic properties, but also in rheological properties [12–15].

The addition of fillers leads to an increase in the viscosity of a compound. Filler, when used in the compounding process, significantly raises the thermal conductivity of the system as a whole. When used, the thermal conductivities of the compound are higher than those of the individual polymers. While using inorganic filler, the thermal conductivity of the compound declines [16].

The aim of mixing in compounding is to homogenise the components, in other words to distribute the melt particles within a given volume, where the melt particles differ in at least one property [7, 8]. When compounding in an extruder there is both distributive and dispersive mixing. Distributive mixing evenly distributes the mixing components, while dispersive mixing reduces the size of agglomerates and then disperses the fragments in the melt. The dispersion of material is the general trend of the two mixing processes.

In compounding, the development of melt temperature is heavily linked to the melting of solid material in the screw channel. The temperature around the granules is important for the melting process. In particle/fluid systems, the shear rate increases as the flow cross-section of the liquid is reduced by the presence of the solid material.

Polymer compounding is an important operation in processing industries. During compounding, the processes of mixing, melting and pumping are carried out. In the extruder, the screw element of the compounding process, the efficiency of compounding may be substantially improved by incorporating mixing sections into the screw design.

In the screw section, the mixing of the polymer and other ingredients can be designed to achieve distributive or dispersive mixing. Compounding can also be improved by optimising process conditions such as back pressure, screw speed and melt temperature. It is the combination of the performance of the mixing equipment and the screw design that leads to optimisation of compounding. To optimise the compounding and equipment performance it is thus essential to evaluate the mixture quality efficiently, which will assist with quality control for the final product [17].

Before compounding, the following important parameters related to optimisation of the compound should be considered:

- The physical state, chemical nature and concentration of the additive;
- The order and site of addition of the feed streams;
- The selection of the mixing configuration, which, in turn, depends on the nature of the additive (low-viscosity liquid, low-MW solid, melt, liquid); and
- The mixing requirements (distributive *versus* dispersive).

6.8 Regrind

When using a regrind step during compounding, several control factors are often overlooked that can result in loss of material, loss of product and even damage to the processing equipment. The use of regrind allows maximum material usage, but the regrind is not exactly the same as virgin material and may negatively affect the process. The maximum regrind allowed for a particular part should be specified for a polymer product.

6.8.1 Regrind Usage in Compounding

The following should be considered:

- It should be free from contamination. Contamination can result from mixing different polymers, non-polymeric materials such as paper, and metal as foreign objects.
- Particle size can have an effect during compounding.

- Small dust, such as particles of regrind, tends to heat up during compounding and degrades quickly because of its small particle mass. While compounding, the small particles cause black specks in the polymer that are visually and mechanically damaging. Such fines can be minimised by setting up screening while loading of the regrind while compounding.

- Fluff is a low-density, fibrous form of regrind that may be introduced as the polymer is 'shaved' or 'skived' from various operations. Fluff changes the regrind density significantly and can also prevent proper mixing of other ingredients while compounding. Fluff, like fines, should be removed prior to compounding.

- All regrind should be compounded with the virgin material by weight only, because the bulk density of the regrind will be different from that of the virgin pellets. Regrind in the final mix can cause variation in the polymer product performance.

The solution of any polymer processing problem requires it to be defined both qualitatively and quantitatively. It is important with polymer compounding to use the polymeric material in an expert way based on knowledge of how to deal with such materials with equipment, especially for practical applications. Polymer compounding is used to develop new products tailored to a particular end use. The effort is mutually profitable to both the supplier and consumer of the polymeric materials, bringing together both technical and economic competence.

6.9 Summary

- Compounding is an operation to uniformly mix or melt polymer and additives.

- Compounding helps, in a targeted way, to improve the productivity, quality and economy of final products.

- Compounding improves processing conditions.
- Compounding can be designed to achieve distributive or dispersive mixing.
- Compounding is an important operation in the majority of processing industries.

References

1. S. Hobbs, *Polymer Engineering & Science*, 1986, **26**, 74.
2. L.A. Utracki in *Polymer Alloys and Blends*, Hanser Publishers, New York, NY, USA, 1989.
3. R.J.M. Borggreve, R.J. Gaymans, J. Schuijer and J.F. Ingen Housz, *Polymer*, 1987, **28**, 1489.
4. J. Lyngaae-Jørgensen, K. Lunde Rasmussen, E.A. Chtcherbakova and L.A. Utracki, *Polymer Engineering & Science*, 1999, **39**, 1060.
5. J. Lyngaae-Jorgensen and L.A. Utracki, *Makromolekulare Chemie – Macromolecular Symposia*, 1991, **48/49**, 189.
6. J.S. He, W.S. Bu and J.J. Zeng, *Polymer*, 1997, **38**, 6347.
7. M. Pahl, *Chemie Ingenieur Techik*, 1985, **57**, 421.
8. M. Pahl, *Chemie Ingenieur Techik*, 1985, **57**, 506.
9. S. Moore and W. Peck in *Proceedings of the Society of Plastics Engineers*, Delware Valley Section, Regional Technical Conference, Cherry Hill, NJ, USA, Society of Plastics Engineers, Bethel, CT, 1–2nd March 1977, p.51.

10. J.A. Biesenberger and D.H. Sebastian in *Principles of Polymerization Engineering*, John Wiley & Sons, New York, NY, USA, 1983.

11. H. Werner in *Devolatilisation of Plastics*, Verein Deutscher Ingenieure VDI-GmbH, Dusseldorf, Germany, 1980; and *Polymer Devolatilization*, Ed., R.J. Albalak, Marcel Dekker, New York, NY, USA, 1996.

12. L. Sun, J.J. Aklonis and R. Salovey, *Polymer Engineering & Science*, 1993, **33**, 1308,

13. S.H. Maron and P.E. Pierce, *Journal of Colloid Science*, 1956, **11**, 80.

14. M. Mooney, *Journal of Colloid Science*, 1951, **6**, 162.

15. T. Kataoka, T. Kitano, Y. Oyanagi and M. Sasahara, *Rheologica Acta*, 1979, **18**, 635.

16. H. Schilling, *Kautschuk und Gummi, Kunststoffe*, 1963, **16**, 2, 84.

17. P.V. Danckwerts, *Applied Scientific Research: Set A*, 1952, **3**, 279.

Abbreviations

ABS	Acrylonitrile-butadiene-styrene
CBA	Chemical blowing agent(s)
FRP	Fibre-reinforced polymers(s)
Gel T_g	Glass transition temperature of the resin at its gel point
HDPE	High-density polyethylene
HDT	Heat distortion temperature
LDPE	Low-density polyethylene
MA	Maleic-anhydride
MMA	Methyl methacrylate
MW	Molecular weight
PA	Polyamide(s)
PBA	Physical blowing agent(s)
PBT	Polybutylene terephthalate
PC	Polycarbonate
PCL	Poly(ε-caprolactone)
PDLLA	Poly(D,L-lactic acid)
PE	Polyethylene
PET	Polyethylene terephthalate
PLA	Polylactic acid
PMMA	Polymethyl methacrylate
PO	Polyolefin(s)
PP	Polypropylene

PPO	Poly(2,6-dimethyl phenylene oxide)
PS	Polystyrene
PVC	Polyvinyl chloride
PVDF	Polyvinylidene fluoride
T_g	Glass transition temperature
T_{g0}	Glass transition temperature of the unreacted resin mixture
$T_{g\infty}$	Glass transition temperature of the fully cured resin
TiO_2	Titanium dioxide
T_m	Melting temperature
UPR	Unsaturated polyester resins
UV	Ultraviolet
WC	Wood composite(s)
WPC	Wood plastic composite(s)
α-mS	α-Methylstyrene

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ISBN: 978-1-90903-060-2

Published by Smithers Rapra Technology Ltd, 2014

Polymer Compounding, Volume 1 focuses on aspects of the raw materials used in polymer processing. Polymer compounding comprises a complex heterogeneous system of polymers and other ingredients and, in many ways, the preparation of these materials is still very much an art. It is a powerful tool that will eventually be required as one of the basics of polymer processing.

This book provides readers with a wide array of state-of-the-art strategies to develop their knowledge about compounding and the use of polymers while minimising wastage during processing. Details about polymer properties and additives are assembled to provide a one-source repository for compounding.

Another important point to be considered in the book is the combination of polymers and additives and the essentials required for the development of economic and environmental incentives in polymer processing.

This book will encourage further studies to understand the scientifically challenging polymer processing issues arising during the manufacture of parts for end-use applications. Finally, this volume presents an overview of polymer compounding requirements, as well as an idea of some of the future directions, advances and challenges of polymer processing.

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