

# Functional Polymers in Food Science From Technology to Biology

# Volume 1: Food Packaging

Edited by Giuseppe Cirillo Umile Gianfranco Spizzirri Francesca Iemma





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# Functional Polymers in Food Science

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# Preface

This book is an extensive and detailed overview of recent developments in the application of functional polymeric materials in food science, with an emphasis on the scientific concerns arising from the need to combine the properties of such versatile materials with nutritional needs. Consumers are increasingly conscious of the relationship between diet and health, and thus the request for high quality and safe foods has been continuously growing. This has resulted in tremendous efforts being undertaken in both academia and industry to increase the quality of food composition and storage. By taking advantage of the contribution of researchers in top universities, industrial research and development centers, this book is meant as a link between scientific and industrial research, showing how the development in polymer science can impact the field.

The book is composed of two volumes; the first concerns the application of polymers in food packaging, while the second shows the relationship between polymer properties, functional food and food processing.

The first volume highlights novel insights in the research on the best performing materials for intelligent packaging, capable of preserving food quality and prolonging product shelf life. After an introduction to the field, the volume goes into a detailed evaluation of the key polymeric and composite materials employed in food packaging for eventually addressing regulation issues.

The second volume opens with an overview of how polymers can be used to improve the quality of food by affecting agricultural processes, and subsequently the food rheology and nutritional profile of novel functional foods and nutraceuticals are extensively developed.

# Polymers and Food Packaging: A Short Overview

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#### Abstract

A discussion on the state-of-the-art performance of biopolymers and functional biopolymers, focusing on food packaging applications, is presented in this chapter. An overview is given of the most important materials used for producing biobased films, their limitations, recycling pattern, and solutions thereof. Furthermore, transport phenomena and regulation concerns are extensively treated.

*Keywords:* Food packaging, functional biopolymers, environmental concerns, regulation issues

# 1.1 Introduction

Packaging materials are widely used to protect the product from its surroundings, retard food product deterioration, and extend shelf life, producing a positive effect on the food quality and safety [1]. A number of packaging materials have been developed to meet these objectives, and considerable efforts have been made to develop the most efficient materials from both a mechanical and a functional point of view.

Apart from the materials used, packaging technology is of great importance. Among the different technologies, High Pressure Processing of Foods is an innovative technology applied for safety assurance, shelf-life extension, and nutrient preservation, and it is known for its potential in

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manufacturing value-added foods, retaining heat-labile nutrients, flavors, and aromas [2].

When considering any potential materials used for packaging, the direct contact between food substances and materials should be tightly controlled, since the migration of low molecular weight additives from packaging material into foodstuffs can occur [3,4]. Several different scientific reports and articles have investigated the migration of compounds such as solvents, reaction byproducts, additives, and monomers from packaging polymers into food [5]. Similarly, considerable attention and concern have been devoted to the evaluation of loss of low molecular weight compounds (including volatile and nonvolatile substances) from a food into polymeric packaging materials [6]. This is of particular importance, since the nonvolatiles, such as fats and pigments, can affect the package itself, while sorption of volatiles (flavors and aromas) more directly affects food quality, such as loss of aroma intensity [7].

Due to its deliberate interaction with the food and/or its environment, the migration of substances could represent a food safety concern, and most active and intelligent concepts that are on the market in the USA and Australia could not be introduced in Europe due to more stringent EU legislation. With regard to this, repealing of the EU Framework Directive 89/109/EEC for food contact materials, resulted firstly in the adoption of a Framework Regulation 1935/2004/EC [8] in which the use of active and intelligent packaging systems are now included. It was only in 2009 that Regulation 450/2009/EC [9] was considered to be a specific measure that laid down rules ad hoc for active and intelligent materials and articles to be applied in addition to the general requirements established in Regulation 1935/2004/EC for their safe use.

Commonly used petroleum-based materials show disposability, easily controlled gas permeability, and durability. On the other hand, these materials are not easy to biodegrade, and generate much heat and exhaust gases when burned, thus posing a global issue of environmental pollution [10].

Analysis of the life cycle of petrochemically-based products allows the understanding of waste management, which is an important issue to every material. After consumer use, the product eventually becomes waste which is either landfilled or recovered in the form of secondary product or by means of energy recovery from an incinerator. Obviously if a product remains in the landfill it contributes to its expansion and to environmental pollution. A new portion of raw material must be extracted from the Earth in order to meet the requirements of consumers or industry. However, recovery gives waste products a chance for a "second life," thus both saving raw material resources and keeping the environment clean and healthy. Packaging is a product with a very short lifetime, counted frequently in weeks. Sixty percent of all packaging is for food products, helping to save large quantities of food which would otherwise be wasted (in some developing countries even 50%) [11].

In addition, petroleum resources are not infinite, and prices are likely to rise in the future. Joint efforts by the packaging and food industries have reduced the amount of packaging, however, packaging creates disposal problems. In the food packaging industry, the use of proper packaging materials and methods to minimize food losses and provide safe and wholesome food products has always been the main interest. Environmental issues have been attracting consumers' attention. Consequently, consumer pressure and rising petroleum prices are encouraging the use of environmentally friendly biodegradable packaging as an alternative to materials produced from nonrenewable resources. Because of this, efforts have been made to utilize raw materials originating from agricultural sources. The use of edible films and coatings is an environmentally friendly technology that offers substantial advantages for an increase in the shelf life of many food products [12].

Biopolymer or biodegradable plastics are polymeric materials in which at least one step in the degradation process is through metabolism of naturally occurring organisms [13]. According to the European Bioplastics Organization, bioplastics can be defined as plastics based on renewable resources or as plastics which are biodegradable and/or compostable. Under appropriate conditions of moisture, temperature, and oxygen availability, biodegradation leads to fragmentation or disintegration of plastics with no toxic or environmentally harmful residue [14,15]. Biopolymers can be broadly divided into different categories based on the origin of the raw materials and their manufacturing processes. They include:

- Biopolymers produced by microbial fermentation like microbial polyesters such as poly(hydroxyalkanoates) including poly(-hydroxybutyrate), poly(3-hydroxybutyrate-co-3-hydroxyvalerate);
- Synthetic biodegradable polymers such as poly(l-lactide), poly(glycolic acid), poly(ε-caprolactone), poly(butylenes succinate), poly(vinyl alcohol), etc.;
- Natural biopolymers such as plant carbohydrates like starch, cellulose, chitosan, alginate, agar, carrageenan, etc., and animal or plant origin proteins like soy protein, corn zein, wheat gluten, gelatin, collagen, whey protein, and casein.

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At present, biodegradable packaging materials have some limitations: for example, they cannot fully match the characteristics similar to petroleumbased materials, and costs are high. Biopolymers alone do not form films with adequate mechanical properties unless they are first treated by either plasticizers, blending with other materials, genetic or chemical modification or combinations of the above approaches. Blends of biopolymers with other biodegradable polymers have been considered a promising avenue for preparing polymers with "tailor-made" properties (functional physical properties and biodegradability). Incorporating relatively low-cost natural biopolymers into biodegradable synthetic polymers provides a way to reduce the overall cost of the material and offers a method of modifying both properties and degradation rates. Food grade plasticizers include glycerol and sorbitol, with glycerol being the most popular plasticizer used in film-making techniques, due to stability and compatibility with the hydrophilic biopolymeric packaging chain.

Recently, a new class of materials represented by bionanocomposites, consisting of a biopolymer matrix reinforced with particles (nanoparticles), with enhanced barrier, mechanical and thermal properties has been considered as a promising option in improving the properties of these biopolymer-based packaging materials [16]. Enhanced barrier properties of the bionanocomposites against  $O_2$ ,  $CO_2$ , water vapor, and flavor compounds would have a major impact on extending the shelf life of various fresh and processed foods. In addition, biodegradability of the bionanocomposites can be finely tuned through the proper choice of polymer matrix and nanoparticles, which is also a driver for the use of bionanocomposites in food packaging.

In the last decades the concept of an "active food packaging system" represents an innovative aspect for packaging materials with respect to some other roles such as an inert barrier to external conditions. Active packaging system involves a positive interaction between the packaging material and the foodstuffs in order to provide desirable effects.

The food package interaction is achieved by the addition of certain additives into the packaging film to enhance the performance of the packaging system [17]. Active packaging techniques can be divided into three categories: absorbers, releasing systems and other systems [18]. Scavenging systems remove undesired components such as oxygen, carbon dioxide, ethylene, humidity. Releasing systems actively add or emit compounds to the packaged food or into the headspace of the package, such as carbon dioxide, antioxidants and preservatives.

The most interesting and promising components of active packaging are antimicrobial and antioxidant species.

Antimicrobial packaging allows industry to potentially combine the preservative functions of antimicrobial agents with the protective functions for foods, and is an efficient and alternative way for using antimicrobial agents for food safety. When antimicrobial activity is conferred to the packaging material, the microbial growth is limited or prevented by reducing growth rate or by decreasing live counts of microorganisms [19,20]. When foodgrade antimicrobial substances are incorporated into polymer, the use of antimicrobial films allows the release of active compounds from the film, and continuous antimicrobial effects take place on the food surface during the exposure time, increasing consumer safety because these compounds are included in the packaging structure instead of being directly added to food, and are released in smaller amounts on the food surface.

Another serious problem in the food industry consists of protecting shelf-stable food from oxidation reactions, which affect the food quality, causing loss of nutritional quality and changes in chemical composition. Due to the presence of unsaturations in their structure, the food components most susceptible to oxidation are fats and oils [21]. Lipid oxidation in the food system causes not only deterioration and reduction in the shelf life, but also affects taste, loss in nutritional value and safety of foods, and development of many chronic diseases [22]. Although conventional antioxidants provide a good protection against oxidative processes, they suffer from some serious limitations. Most of the antioxidants currently used in the industry are low molecular weight compounds and processes such as evaporation, diffusion and leaching can affect their performance [23,24]. The physical loss decreases the effective protective capabilities of the antioxidants, resulting in processed food being unprotected against oxidation after a short period of time.

During the past decade several attemps have been made to substitute the low molecular weight antioxidants with higher molecular weight products (antioxidant polymers) with the objective of achieving longevity and better performance of these materials.

Antioxidant polymers, indeed, couple the advantages of both polymeric and antioxidant systems. They can be obtained by the covalent conjugation of polymers with small antioxidant compounds or by direct polymerization of the same antioxidants [25].

Chemical or enzymatic reactions can be employed for their synthesis and the resulting materials maintain the antioxidant properties of the antioxidant moiety and, at the same time, acquire the good stability properties of the macromolecular systems [26–28].

In this volume, we provide an overview on food packaging based on biopolymers and functional biopolymers. The most important materials

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used for producing biobased films, their limitations, recycling pattern, and solutions thereof are treated together with the transport phenomena and the regulation concerns in the field.

# References

- 1. Zhang, H., Mittal, G. Biodegradable protein-based films from plant resources: A review. *Environmental Progress & Sustainable Energy* 29:203–220, 2010.
- Koutchma, T., Song, Y., Setikaite, I., Juliano, P., Barbosa-Canovas, G. V., Dunne, C. P., Patazca, E. Packaging evaluation for high-pressure high-temperature sterilzaition of shelf-stable foods. *Journal of Food Process Engineering* 33:1097–114, 2010.
- 3. Huang, C., Zhu, J., Chen, L., Li, L., Li, X. Structural changes and plasticizer migration of starch-based food packaging material contacting with milk during microwave heating. *Food Control* 36:55–62, 2014.
- 4. Arab-Tehrany, E., Mouawad, C., Desobry, S. Determination of partition coefficient of migrants in food simulants by the PRV method. *Food Chemistry* 105:1571–1577, 2007.
- 5. Baner, A., Bieber, W., Figge, K., Franz, R., Piringer, O. Alternative fatty food simulants for migration testing of polymeric food contact materials. *Food Additives and Contaminants* 9:137–148, 1992.
- Giacin, J. R. Factors affecting permeation, sorption, and migration processes in package-product systems. In *Foods and Packaging Materials-Chemical Interactions*, ed. Ackermann, P., Jägerstad M., Ohlsson, T., pp. 12–22. Cambridge, Great Britain: The Royal Society of Chemistry, 1995.
- 7. Sadler, G. D., Braddock, R. J. Oxygen permeability of low-density polyethylene as a function of limonene absorption: An approach to modelling flavour scalping. *Journal of Food Science* 55:587–588, 1990.
- 8. The Commission of the European Communities. Regulation (EC) No. 1935/2004 of the European Parliament and of the Council of 27 October 2004 on materials and articles intended to come into contact with food and repealing Directives 80/590/EEC and 89/109/EEC. *Official Journal of the European Union*, L338, 2004.
- 9. The Commission of the European Communities. Commission Regulation (EC) No. 450/2009 of 29 May 2009 on active and intelligent materials and articles intended to come into contact with food. *Official Journal of the European Union*, L135, 2009.
- 10. Barlow, C. Y., Morgan, D. C. Polymer film packaging for food: An environmental assessment. *Resources, Conservation and Recycling* 78:74–80, 2013.
- 11. Kozlowski M., ed., *Plastics Recycling in Europe*, Ofic. Wyd. Pol. Wr., Wroclaw, 2006.

- 12. Tang, X. Z., Kumar, P., Alavi, S., Sandeep, K. P. Recent advances in biopolymers and biopolymer-based nanocomposites for food packaging materials. *Critical Reviews in Food Science and Nutrition* 52:426–442, 2012.
- Peelman, N., Ragaert, P., De Meulenaer, B., Adons, D., Peeters, R., Cardon, L., Van Impe, F., Devlieghere, F. Application of bioplastics for food packaging. *Trends in Food Science and Technology* 32:128–141, 2013.
- 14. Chandra, I., Rustgi, R. Biodegradable polymers. *Progress in Polymer Science* 23:1273–335, 1998.
- Reddy, M. M., Vivekanandhan, S., Misra, M., Bhatia, S. K., Mohanty, A. K. Biobased plastics and bionanocomposites: Current status and future opportunities. *Progress in Polymer Science* 38:1653–1689, 2013.
- Sorrentino, A., Gorrasi, G., Vittoria, V. Potential perspectives of bionanocomposites for food packaging applications. *Trends in Food Science and Technology* 18:84–95, 2007.
- 17. Robertson, G. L. *Food packaging: Principles and Practice*. 2nd ed. London: CRC Press, 2006.
- 18. Ahvenainen, R. *Novel Food Packaging Techniques*. Woodhead Publishing Limited, Cambridge: England; 2003.
- Galotto, M. J., Valenzuela, X., Rodriguez, F., Bruna, J., Guarda A. Evaluation of the effectiveness of a new antimicrobial active packaging for fresh Atlantic Salmon (Salmon Salar L.) shelf life. *Packaging Technology and Science* 25:363– 372, 2012.
- Mastromateo, M., Danza, A., Conte, A., Muratore, G., Del Nobile, M. A. Shelf life of ready to use peeled shrimps as affected by thymol essential oil and modified atmosphere packaging. *International Journal of Food Microbiology* 144:250–256, 2012.
- 21. Benzie, I. F. F. Lipid peroxidation: A review of causes, consequences, measurement and dietary influences. *International Journal of Food Science and Nutrition* 47:233–261, 1996.
- 22. Eriksson, C. E. Oxidation of Lipids in Food Systems: Autoxidation of Unsaturated Lipids. Academic Press Inc.: London, 1987.
- Cirillo, G., Vittorio, O., Hampel, S., Spizzirri, U. G., Picci, N., Iemma, F. Incorporation of carbon nanotubes into a gelatin-catechin conjugate: Innovative approach for the preparation of anticancer materials. *International Journal of Pharmaceutics* 446 (1–2):176–182, 2013.
- Iemma, F., Trombino, S., Puoci, F., Cirillo, G., Spizzirri, U. G., Muzzalupo, R., Picci, N. Synthesis and antioxidant efficiency of a new copolymer containing phosphorylated myo-inositol. *Macromolecular Bioscience* 5:1049–1056, 2005.
- Cirillo, G., Curcio, M., Vittorio, O., Iemma, F., Restuccia, D., Spizzirri, U. G., Puoci, F., Picci, N. Polyphenol conjugates and human health: A perspective review. *Critical Reviews in Food Science and Nutrition*. DOI: 10.1080/10408398.2012.752342, 2014.

- 8 FUNCTIONAL POLYMERS IN FOOD SCIENCE
- Spizzirri, U. G., Parisi, O. I., Iemma, F., Cirillo, G., Puoci, F., Curcio, M., Picci, N. Antioxidant-polysaccharide conjugates for food application by ecofriendly grafting procedure. *Carbohydrate Polymers* 79:333–340, 2010.
- 27. Spizzirri, U. G., Cirillo, G., Curcio, M., Altimari, I., Picci, N., Iemma, F. Stabilization of oxidable vitamins by flavonoid-based hydrogels. *Reactive and Functional Polymers* 73:1030–1037, 2013.
- Cirillo, G., Puoci, F., Iemma, F., Curcio, M., Parisi, O. I., Spizzirri, U. G., Altimari, I., Picci, N. Starch-quercetin conjugate by radical grafting: Synthesis and biological characterization. *Pharmaceutical Development and Technology* 17:466–476, 2012.

# **Polymers for Food Shelf-Life Extension**

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#### Abstract

The shelf life of food is of interest to everyone in the food chain, from producer to consumer. Factors affecting shelf life include microbiological, chemical, biochemical and sensory changes during storage.

The shelf life of a food is controlled by many factors and the packaging is one of the most important factors which affect food preservation.

Without developments in packaging, food harvesting, processing and distribution systems would not have been developed to their present levels, consumers would not have easy access to the wide range of foods offered today, and food waste due to spoilage, damage and loss would be high. Packaging, then, is an integral part of the food industry. The objective of this chapter is to describe the shelflife concept, to examine the main factors influencing it and the main tests utilized for monitoring shelf life, to introduce the role of different typologies of packaging and to explain some innovative polymers for food packaging applications. Finally, the chapter closes with a section on the future trends in food packaging.

Keywords: Shelf life, food packaging, innovative polymers

# 2.1 Shelf-Life Concept

To introduce the concept of shelf life it is necessary to recall the concept of "principle of food degradation." This principle states that all foods are subjected over time to a progressive transformation of their chemical, physical

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and organoleptic microbiological and structural properties [1]. Shelf life is closely related to the durability of a food that can be expressed as:

- "Use before" dates on food that goes off quickly, such as smoked fish, meat products and ready-prepared salads. Any food or drink should not be used after the end of the "use by" date on the label, even if it looks and smells fine. This is because using it after this date could put your health at risk;
- "Best before" dates appear on a wide range of frozen, dried, tinned and other foods.

The "best before" dates are more about quality than safety, except for eggs. So when the date runs out it does not mean that the food will be harmful, but it might begin to lose its flavor and texture. The "best before" date will only be accurate if the food is stored according to the instructions on the label, such as "store in a cool dry place" or "keep in the fridge once opened." The food supplier is responsible for placing a use by or best before date on food.

All foods are in fact systems of great complexity from the chemical, chemical-physical and biological point of view. In particular, food is an ecosystem:

- COMPLEX, characterized by a community microbial (i.e., set of bacterial populations different) essentially determined from the raw materials used and the process production/ preparation put in place;
- DYNAMIC, evolving during storage for the effect of intrinsic factors (e.g., pH, a<sub>w</sub>) and extrinsic (e.g., temperature, preservation conditions).

Because of the complexity and dynamism of system "food," the quality of a food product is a dynamic attribute that starting from the time of its production, moves—continuously and inexorably—toward ever lower levels. Thus representing the decay of quality of a product in a Cartesian plane where in the Y-axis is reported the level of quality and in the X-axis the time, a curve is obtained whose shape is a function of the type of considered product.

Extreme cases are canned foods and vegetables, in which the deterioration can be represented more correctly by a straight line with minimum slope, and opposite the vegetables are represented by a straight line with a slope which is very accentuated, respectively (Figure 2.1).

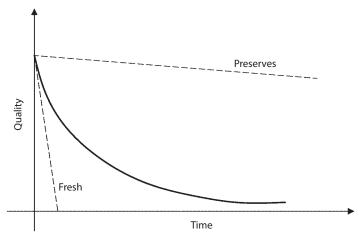


Figure 2.1 Decay of quality of a product in function of time of life.

# 2.2 Shelf-Life Definitions

There are many definitions of shelf life of a food, among the most used are:

- Shelf life is that period of time which corresponds, under certain conditions of storage, to a tolerable decrease in the quality of the food [2].
- Shelf life is, under certain conditions of storage, the time limit within which the progress of individual events determines reactive changes imperceptible on the sensorial, or otherwise still acceptable in terms of safety of use [3].

It is interesting to note that in the two different cited definitions the same expression, "under certain preservation conditions," appears, even if they are attributable to two different sources.

This assertion is of principal importance since the concept of shelf life, i.e., the durability or shelf life, is closely related to the storage temperature of the food itself.

In addition to the storage conditions (temperature, but also relative humidity, exposure to light) the shelf life of a product is affected by:

• Microbiological quality of raw materials (level of contamination, type of contamination, growth characteristics of microorganisms);

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  - Formulation of the product (quantity and composition of the used ingredients);
  - Terms of process/method of preparation;
  - Methods of packaging.

Studies of shelf life are required by food regulations. Indeed there are several rules provided to food business operators for checking the durability of their products: Reg 2073/2005, the State-Regions Agreement of 13/01/2005, EC Regulation 852/2004, just to name a few.

Given that a food product is characterized by complexity and dynamism it is evident that the decay of quality characteristics of a food cannot be measured or expressed only by a parameter, but it must be represented by a series of deteriorative changes that are closely linked:

- Microbiological deteriorative changes;
- Chemical and biochemical deteriorative changes;
- Physical deteriorative changes;
- Temperature-related deteriorative changes.

No single intrinsic factor may determine the shelf life of a food, but the most important to be considered in shelf-life studies are [4]: moisture and water vapor transfer; pH value and total acidity; redox potential (Eh); available oxygen; nutrients; microbiological changes; chemical or biochemical changes; and utilization of preservatives in product formulation. Intrinsic factors are influenced by such variables as raw material type and quality, and product formulation and structure.

Extrinsic factors are those factors the packed product encounters during shelf life and can be listed as: pressure in the headspace; temperature control during storage and distribution; relative humidity (RH) during processing; storage and distribution; exposure to light (UV and IR) during processing, storage and distribution; environmental microbial counts during processing; composition of atmosphere within packaging; subsequent heat treatment (e.g., reheating or cooking before consumption); and consumer handling.

A combination of intrinsic and extrinsic factors, which individually are unable to prevent spoilage, can carry out some changes to the product's sensory and nutritional properties.

## 2.2.1 Microbiological Deteriorative Changes

Ecological factors that influence the behavior of microorganisms in food, and therefore the fate of the microbial community initially present, are classified into four main groups: intrinsic factors, extrinsic factors, processing conditions and implied factors.

Intrinsic factors relate to the characteristics of the food and make reference to the chemical composition, the availability of free water  $(a_w)$ , pH, presence of antimicrobial preservatives, the oxidation-reduction potential, etc.

Extrinsic factors affecting the growth of microorganisms in food are represented by the external conditions applied to the food and relate, in particular, to the temperature, humidity and the gaseous composition of the atmosphere in which the food is stored.

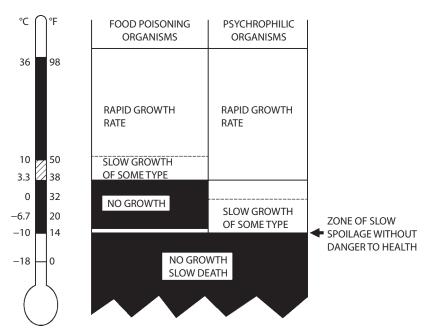
The processing conditions include all those procedures which applied to the food during its transformation, change all the ecology. The technological processes applied may include heat treatment, refrigeration, salting, acidification, addition of starter cultures and so on.

The implied factors include the relationships that develop between the microorganisms that have colonized the food. Microbial populations present in the food may exert synergistic actions, (a given group of organisms is benefited by the development of another group, e.g., removing toxic metabolites, or producing useful metabolites, or by changing the intrinsic conditions of the food) and antagonistic actions (a group of microorganisms becomes dominant over the other for different reasons, such as the production of antimicrobial substances, or through competition for nutrients, etc.).

Temperature is the most efficient means of controlling microbial growth (Figure 2.2). Each microorganism is characterized by an optimum value of growth temperature, from a minimum and a maximum value, when it is in ideal conditions of development relative to other factors. Based on this parameter, microorganisms are roughly classified as reported in Table 2.1.

The high temperatures, higher than the maximum growth, exert a microbicide action. The sensitivity of microorganisms to high temperatures, which represents precisely the heat resistance, varies in relation to several factors, in particular:

• The water and the free water (a<sub>w</sub>): in the absence of water the RTD increases because the proteins require a higher temperature for denaturation.



**Figure 2.2** Low temperature limits growth of food poisoning and food spoilage organisms [5].

Microorganism	Minimum (°C)	Optimum (°C)	Maximum (°C)
Psychrophies	-5	0	30
Psychrotrophs	0	15-25	37
Mesophiles	10	30-37	45
Thermotrophs	20	45	50
Thermophiles	40	55	65

 Table 2.1 Classification of microorganisms based on growth temperature.

- The pH: microorganisms are more resistant to high temperatures at their optimal pH for growth, which is generally around 7; at acid and alcalin pH the heat resistance drops.
- The substances that exert a protective action, such as fats, carbohydrates, proteins, colloids and other salts, increase the heat resistance.
- The number of microorganisms: the greater the number of microorganisms, the higher the degree of heat resistance.

- The age of the cell: the maximum resistance occurs at the beginning of the lag phase. The cells in the stationary phase are more heat resistant than those in phase logarithmic (young cells).
- The temperature of maximum growth: for the same microorganism, the heat resistance increases with the increase of its growth temperature.
- Inhibitory substances: the heat resistance decreases in the presence of inhibitory antibiotics, CO<sub>2</sub>, SO<sub>2</sub>, etc.

The low temperatures are distinguished in refrigeration (between 0 and  $+5^{\circ}$ C) and freezing temperatures (between -40 and  $0^{\circ}$ C and more). The low temperatures primarily exert bacteriostatic action on microorganisms, and only in small part bactericidal action [6,7].

The temperature decrease slows or stops the growth when the enzyme activity is blocked by the water unavailability.

Within the growth range, the rate of growth increases rapidly as the temperature is raised (Figure 2.3). Conversely, microbial growth rates decrease rapidly as the temperature is lowered and, hence, food spoilage occurs much more slowly. This effect is especially marked near the freezing point. Note in Figure 2.4 that a drop from about 16°C to about 0°C will more than double the shelf life (time before spoilage).

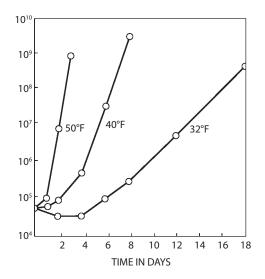


Figure 2.3 Growth of bacteria on chicken at three temperatures [8].

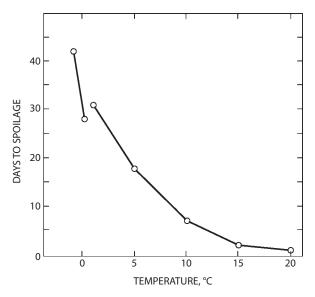


Figure 2.4 Effect of temperature on time for chicken meat to spoil [9].

The free water a<sub>w</sub> determines the hygiene and stability of the food with respect to microbial growth, the rate of chemical reactions and physical properties.

The  $a_w$  indicates the amount of water, within the total water of the food, available for the growth of microorganisms. Each species of microorganism (bacterium, yeast, mold) has its minimum, optimum and maximum  $a_w$ , value below which no growth is possible. This value corresponds to the survival power of the various microorganisms. With the measure  $a_w$  of a food you can determine which organism is able or not to develop into a food. The values of  $a_w$  development limits are 0.91 to 0.95 for the majority of bacteria, 0.88 for most yeasts or 0.80 for osmosis tolerant yeasts; 0.75 for halophilic bacteria.

The a<sub>w</sub> limit that prevents the development of most pathogens is 0.90, for tolerant molds 0.70, and for all organisms is 0.60.

A<sub>w</sub> measurement makes it possible to:

- Predict which microorganism could be the potential source of infection or alteration;
- Maintain the chemical stability of the food;
- Minimize the nonenzymatic browning reactions and oxidation reactions catalyzed spontaneously;
- Extend the activity of enzymes and vitamins;

• Optimize the physical properties of foods such as migration of moisture, texture and shelf life.

pH is a term used to describe the acidity or alkalinity of a solution. At pH 7, there is an equal amount of acid (hydrogen ion: H+) and alkali (hydroxyl ion: OH-), so the solution is "neutral." pH values below 7 are acidic, while those above 7 are alkaline. The pH has a profound effect on the growth of microorganisms. Most bacteria grow best at about pH 7 and grow poorly or not at all below pH 4. Yeasts and molds, therefore, predominate in low pH foods where bacteria cannot compete. The lactic acid bacteria are exceptions; they can grow in high acid foods and actually produce acid to give us sour milk, pickles, fermented meats, and similar products. Some strains, called Leuconostoc, contribute to impart off-flavors to orange juice.

In Table 2.2 intrinsic and extrinsic factors affecting the growth of some key pathogens and spoilage organisms are shown. It is important to note that this table lists approximate growth limits with the various factors acting alone without considering eventually interactions between them.

Moreover, raw material used by the food industry, represents a potential source of microbial contamination. The potential growth of pathogens and spoilage flora will be affected by the initial level of contamination and the efficacy of processing steps in eliminating bacteria in the food. A better quality of raw material in terms of microbial contamination can be obtained with more stringent controls on primary production and sampling. With a good initial quality of raw materials, the shelf life of food could be extended.

### 2.2.2 Chemical and Biochemical Deteriorative Changes

The chemical and biochemical reactions that happen during the transformation and preservation of food include: nonenzymatic browning, enzymatic browning, lipid hydrolysis, lipid oxidation, hydrolysis of proteins, protein denaturation, agglomeration of the protein, hydrolysis of polysaccharides, glycolysis, synthesis of polysaccharides, degradation of natural pigments, inactivation of vitamins, changes in the bioavailability of vitamins and minerals.

Air and oxygen are both direct and indirect causes of food degradation. Oxygen acts directly by oxidizing some vitamins (A and C), some aromatic substances and pigments. The phenomenon of the darkening of apples, once cut, is due to the action of oxygen in contact with the pulp of the fruit.

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Type of microorganism	Minimum pH for growth	Minimum a <sub>w</sub> for growth	Anaerobic growthª	Minimum growth temp. <sup>b</sup> (°C)
Pathogens <sup>c</sup>				
Salmonella	4.0	0.94	Yes	7.0
Staphylococcus aureus	4.0 (4.5 for toxin)	0.83 (0.90 for toxin)	Yes	6.0 (10 for toxin)
Bacillus cereus (psychrotrophic)	4.4	0.91	Yes	<4.0
Clostridium botulinum				
Proteolytic A, B, F	4.6	0.93	Yes	10
Non-proteolytic B, E, F	5.0	0.97	Yes	3.3
Listeria monocytogenes	4.3	0.92	Yes	0.0
Escherichia coli	4.4	0.95	Yes	7.0
Vibrio parahaemolyticus	4.8	0.94	Yes	5.0
Yersinia enterocolitica	4.2	0.96	Yes	-2.0
E. coli 0157	4.5	0.95	Yes	-6.5
Spoilage organisms <sup>d</sup>				
Pseudomonas	5.5	0.97	No	<0
Enterobacter aerogenes	4.4	0.94	Yes	2.0
Lactic acid bacteria	3.8	0.94	Yes	4.0
Micrococci	5.6	0.90	No	4.0
Yeasts	1-5	0.80	Yes	-5.0
Moulds	<2.0	0.60	No	<0

 Table 2.2
 Minimum growth conditions for selected microorganisms.

<sup>a</sup> Survival without oxygen, for example in vacuum pack.

<sup>b</sup> Minimum growth temperatures are for growth in typical neutral pH. High water activity, chilled foods.

<sup>c</sup> Data for pathogens taken from Anon., *Harmonisation of Safety Criteria far Minimally Processed Foods*. Inventory Report, Fair Concerted Action FAIR CT96-1020, 1997.

<sup>d</sup> Data for spoilage organisms taken from Brown, H. M., *Evaluahon of the Shelflife of Chilled Foods.* Campden and Chorleywood FRA Technical Manual No. 28, 1991.

The rate of deterioration of a food is different according to the type and the environmental conditions in which it is located; in meat, fish, milk, eggs, for example, the process of spoilage occurs very quickly and their conservation is reduced to a few days in a cool place but just a few hours in warm climates.

Oxidative rancidity is considered the most serious and frequent alteration of dietary fat. The process is essentially chemical in nature and takes place in three phases: a phase of initiation or induction, in which they develop radicals, a center stage of propagation and a termination phase where the radicals are stabilized with formation of various organic compounds.

Among these there are volatile aldehydes and ketones responsible for the rancid odor. The alteration is favored in the initial stages by the competition of some environmental factors, including exposure to light, high temperatures, the presence of peroxides, the contact or the presence of certain metals (including iron and copper), and the presence of the lipoxidase enzyme. A fundamental role is played by the presence, in the food, of compounds that slow the initiation phase (antioxidants such as tocopherols) or promote it (pro-oxidants such as myoglobin, hemoglobin and chlorophyll). The arrangement, however, is the result of a complex set of factors that can protect food or expose it to more of this alteration.

Also, the light can react with some compounds contained in foods, such as vitamins A, B2, C, and with some fat or proteins, by changing the color of the food itself. For example, almost any type of food processing or storage causes some deterioration of the chlorophyll pigments. This reaction is accelerated by heat and is acid catalyzed. Because of this it is opportune to keep certain foods at risk in dark containers (beer, wine). Other reactions are also possible. For example, dehydrated products such as green peas and beans packed in clear glass containers undergo photo-oxidation and loss of desirable color [10].

Finally, in some foodstuffs, compounds derived from long-chain fatty acids play an extremely important role in the formation of characteristic flavors that can lead to significant off-flavors. In this case, the permeability of packaging materials is of importance for retaining desirable volatile components within packages, or in permitting undesirable components to permeate through the package from the ambient atmosphere.

# 2.2.3 Physical Deteriorative Changes

The processes of a physical-chemical nature include the crystallization of sugars, starch retrogradation, loss of volatile substances, changes in the partitioning of components, adsorption and desorption of moisture. This last process represents the major cause of physical deterioration of food.

Dehydration causes the wilting of vegetables and the "burn" of frozen vegetables (the whitish spots more or less extensive).

The absorption of moisture damages all dried foods or those with low water content: dry products such as breakfast cereals and biscuits can lose their crispness through moisture uptake, dehydrated foods in powder form lumps, and dried vegetables change taste and color. In addition, excessive humidity favors the development of microorganisms, hydrolytic rancidity of fats and the action of enzymes.

The absorption of moisture is a consequence of an inadequate barrier provided by the package; this results in caking. It can occur either as a result of a poor selection of packaging material in the first place, or failure of the package integrity during storage.

Also, the migration phenomena can limit the sensory shelf life. For example, migration of external volatiles into the food can result in the development of taint. Migration of chemical components from the packaging material can also produce taints, and this can be particularly serious in products with a long shelf life.

# 2.2.4 Temperature Related Deteriorative Changes

Deterioration can occur at both elevated and depressed temperatures. The minimum growth temperatures for a range of pathogens and spoilage organisms outlined earlier illustrates the importance of effective temperature control in preventing microbial contamination and spoilage. Increasing the temperature generally increases the rate of chemical reactions that may result in deterioration. In foods containing fats, more solid fat will become liquid and act as a solvent for reactions in the oil phase, and changes in fat crystallinity can occur, for example, producing bloom in chocolate. Increased temperature can also change the crystallization characteristics of foods containing sugar syrups.

Destabilization of emulsion systems can also occur under conditions of fluctuating temperature or mechanical agitation. Fluctuating temperatures can cause ice crystal formation in frozen foods such as ice cream. In contrast, increased temperatures can reduce the development of staling in bread, although the situation with other baked foods can be complex and unpredictable.

# 2.3 Measuring Shelf Life

There are many methods for determining the shelf life of different food products including microbiological, chemical and sensory evaluation. Different factors will affect the length of shelf life depending on the product, packaging and conditions surrounding the product. Shelf-life testing can be carried out during development and pilot-scale production of the product but should always be carried out once full-scale production has been reached.

# 2.3.1 Sensory Analysis for the Evaluation of Food Shelf Life

Until recently, the food industry defined the quality of products mainly based on the analysis of chemical, physical and microbiological testing, and only secondarily on the judgment of expert tasters of the product. This "physical" procedure, by itself, however, is not capable of effectively representing the views of consumers, the real beneficiaries of the product in question. The purpose of sensory analysis is to identify and objectively describe the sensory properties of a product using a panel of judges adequately educated and trained in order to predict the acceptability of the consumer and assess the "sustainability" of the production choices, as well as the communication of product quality. To achieve this goal the following steps must be taken: identification of the characteristics that describe the sensory quality of the product "fresh" (standard); identification of the level at which the sensory quality remains unchanged compared to the standard (expected product); assessment of the level at which the stored product shows changes in the sensory quality while remaining still acceptable (area of acceptability); determination of the point at which the product has undergone substantial changes in the sensory quality so that it is no longer edible (end point).

The approach of a sensory study involves the following steps:

- Selection of the "standard product" (used as a comparison sample);
- Definition of the storage conditions (ideal, actual, extreme);

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- Choosing of the samples to submit to the shelf-life study (representative of the production and, possibly, of its variability);
- Definition of the timing of the control (time zero or base, at least two intermediate points, end point expected);
- Planning of the sample size (depending on the time of the inspection, storage conditions, for example, at different temperatures, the type of sensory test).

The tests used to analyze sensory characteristics can be classified according to the achievement of the type of information wanted and the complexity of the method, and thus according to the different degree of training of the panel.

The qualitative discriminating tests are able to establish whether a perceptible sensory difference exists between the two products without estimating the magnitude of the difference. These types of tests are widely used for the simplicity of the experimental procedure, the speed with which information is obtained and the sensitivity for small differences between products on the basis of comparative judgments.

The discriminant quali-quantitative methods allow the assessment of sensory differences between multiple samples.

The descriptive methods are used to describe and quantify the sensory characteristics perceived in a product. The descriptive analysis may cover all the sensations detected in the evaluation of a product, or just a few. The different descriptive methods are divided into four main phases:

- a) Definition of the vocabulary of sensory descriptors of the product concerned (qualitative analysis);
- b) Development of reference standards for each descriptor, corresponding to the maximum intensity on the rating scale used;
- c) Assessment of the intensity of each descriptor in the product concerned (quantitative analysis);
- d) Statistical analysis and interpretation of results.

Dynamic tests consider the dynamics of the perception of our senses and are able to record the change with the help of sensory technology.

These methods, time intensity (TI) and temporal dominance of sensations (TDS), make use of specific software, which allows the investigation and recording of the changing perceived sensations, their intensity and their duration. In the TDS sensory profile complex foods can be decomposed to follow in time the attribute or attributes that have the greatest impact on our senses, or alternatively, in the TI sensory profile one can focus on a single characteristic of the product and follow the perception in the course of the tasting.

Dynamic methods can be good solutions to make a "screening" sensory and highlight interesting aspects for further analysis. Moreover, they represent alternative means of investigation alongside classical descriptive analysis.

Discriminatory qualitative tests are used to determine whether a perceptible sensory difference exists between products without estimating the magnitude of the differences.

These types of tests are widely used for the simplicity of the experimental procedure, the speed with which information is obtained and the sensitivity for small differences between products on the basis of comparative judgments. They are effective in Quality Control to assess whether any differences can be perceived due, for example, to changes in the supply of raw materials, in the process, in the type of packaging, in the storage conditions, etc. They can also be used in the early stages of selection, training and monitoring of the judges of the panel.

# 2.3.2 Instrumental Methods

Instrumental methods are used to study and characterize the properties of foods and their constituents during shelf life. These analytical procedures are used to provide information about a wide variety of different characteristics of foods, including their composition, structure, physicochemical properties and sensory attributes.

The evaluation of shelf life of the foodstuff is a critical area in modern production and distribution, first of all in what concerns the products defined as fresh or fresh-like, where the packaging has a decisive role on the maintaining of quality characteristics.

The study of shelf life is divided into five basic steps:

- a) Identification of the most important quality attributes (e.g., decrease of the content of vitamins, changes in the flavor profile, increase in the microbial load, oxidation reactions) that are also easy to monitor over time;
- b) Development of a procedure to control reliability and repeatability over time;

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- c) Study of a protocol of simple and effective action;
- d) Assessment of the relationship cost/benefit ratio;
- e) Verification of the dependence of the degradation reactions from the packing.

Initially the quality attributes monitoring is chosen, which may, for example, be the attribute that we want to be preserved longer, or the one that deteriorates more quickly, or even one dictated by law.

Finally the suitable instrumental method is utilized in order to monitor it over time.

For example, image analysis and the application of the electronic nose are promising and suitable methods for these studies: they objectively investigate and parameterize sensorial indices (appearance, color and aromatic fingerprint), i.e., the most relevant factors for the choice and the consumption of foodstuff. In some case studies, these techniques are used for the evaluation of shelf life of fresh-like vegetables, the investigation on the freshness evolution of dairy products, and the discrimination of predictive effects of different storage technologies of some products with aromatic impact (fish and coffee). Clearly apparent from these studies is the immediate applicability of the results obtained by the use of these techniques, their potentiality on the *in-situ* quality control and on the compelling planes of sampling, and the possibility to characterize multisensory strategies for the definition of shelf life based on the pattern identification methods.

In Table 2.3 the suitable instrumentations to monitor some of the significant variables during shelf life are shown.

### 2.3.3 Physical Measurements

The most commonly used physical tests measure the changes in the texture of products. These changes may be the result of chemical reactions occurring in the product, such as those caused by interaction of ingredients or by environmental influences, such as moisture migration through the packaging. Methods of measurement of texture have to be chosen carefully so that the results correlate well with the textural changes as perceived by the use of sensory panels. Various instruments are available for texture measurement and instrumental methods of measuring attributes such as hardness, crispness and snap are commonly used during shelf-life testing. Some attributes, such as hardness, can be measured relatively easily by measuring the force required to penetrate a particular distance into the product. However, even in simple cases, the details of the tests, such as type

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		Food safe	Food safety and stability			Food quality			Instrument type
	Microbial	Chemical	Physical aspects	Nutritional	Appearance	Texture	Aroma	Taste	
	aspects	aspects		aspects		consistency			
Colour					х				Ultraviolet, visible, near
Sorting by colour	х	х	х	х	х	х	х	х	infrared light detector;
									optical imaging;
Temperature	х	х	х						Thermocouples; resis-
Temperature-time	x	х	х	x	x	x	х	х	tance thermometers;
integral									near infrared detector;
									fibre-optic probe with
									fluorescent tip;
Particle, droplet or			x		x	x			Radiowave detector;
bubble size									ultrasound;
Solid/liquid ratio and			х		x	х			Nuclear magnetic
crystal size									resonance (NMR);
									ultrnsound;
Bulk density			x		x	x			Mechanical resonance
									dipstick, gammarays;
									ultrasound;
Rheology			х		х	х			Capillary viscometers;
									rotary viscometers;
									rheometers.

 Table 2.3
 Selected measurement variables and instrumental types.

		Food safe	Food safety and stability			Food quality			Instrument type
	Microbial	Chemical	Physical aspects	Nutritional	Appearance	Texture	Aroma	Taste	
	aspects	aspects		aspects		consistency			
Texture						х			Puncture/penetration
									devices; shearing
									and cutting devices;
									compression devices;
									flow and mixing
									devices; tenderometer,
									rheometer;
Water activity/content/	x	х	x	x	х	x		х	Near infrared detector;
quality									microwaves; electrical
									conductivity;
Proximates: fat, protein,				x	x	х	x	х	Near infrared detector;
carbohydrates, ash									microwaves;
ЬН	х	х					х	х	Electrometric devices;
									biosensors;
									immun osensors;
Acidity				x			х	х	Biosensors;
									immunosensors;
Sodium, potassium,				х				х	Radiowave detector;
calcium									
Humidity	Х		х		х	х			Hygrometer, capacitance.
Source: E. Kress-Rogers, Technology, Second.	rs, Instrumen	itation and Si	ensors for the Fc	ood Industry. C	Cambridge: Woc	dhead Publish	ing 1993	; P. Fe	Instrumentation and Sensors for the Food Industry. Cambridge: Woodhead Publishing 1993; P. Fellows, Food Processing

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of probe, crosshead speed, sample position and alignment and distance of penetration need to be chosen carefully to obtain the best possible correlation with sensory measurements. More sophisticated methods are also being developed, such as nondestructive tests for online texture measurement, the measurement of sound as a measure of textural attributes and methods for measuring difficult attributes such as stickiness.

Understanding the structure of food is vital in predicting how it will taste and how it will react during preservation. Many methods for the characterization of the texture of food and food ingredients can be used; some of them are reported below.

Rheology

- Measurement of viscoelastic properties of food systems such as bread, pastry and biscuit doughs and other food materials.
- Fluid rheology of wafer and cake batters, gels and dispersions, flavors, yogurts, mayonnaise and so on.
- Generation of viscosity flow curves from –10 to 120°C and calculation of n and K values.
- Fundamental rheological measurements allowing interlaboratory comparisons.

Thermal analysis by differential scanning calorimetry

- Heat flow changes associated with physical changes in state, for example, melting properties. Also gives a measure of the liquid to solid ratio of plastic shortenings.
- Determination of starch gelatinization or "degree of cook" in cereal-based foods.
- Measurement of the rates of staling and the effectiveness of antistaling enzymes and emulsifiers in baked and extruded products.
- Fat melting profiles and crystallization properties.
- Specific heat capacity measurements for engineering calculations.

Emulsifier properties

- Interfacial properties of surfactants/emulsifiers as they occur in foams, emulsions, batters and liquid systems, carried out by interfacial tension and rheology measurements.
- Foaming behavior of emulsifiers.

# 2.3.4 Chemical Measurements

There are usually a number of different analytical techniques available to determine the decay of a food material. It is therefore necessary to select the most appropriate technique for the specific application. The analytical technique selected depends on the property to be measured, the type of food to be analyzed, and the reason for carrying out the analysis. Information about the various analytical procedures available can be obtained from a number of different sources. The following techniques in chemical analysis of food can be applied:

- Enzymatics
- Gas Chromatography–Mass Spectrometry–Mass Spectrometry (GC-MS/MS)
- High-Performance Liquid Chromatography Thermal Energy Analyzer (HPLC-TEA)
- Liquid Chromatography–Mass Spectrometry–Mass Spectrometry (LC-MS/MS)
- Ultraviolet-Visible (UV/VIS) Spectroscopy
- Scanning Electron Microscopy
- Microscopy
- Atomic Absorption Spectroscopy (AAS), Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES)

Some chemical tests determining changes in a particular quality characteristic can be applicable to different types of products.

# 2.3.5 Microbiological Measurements

The microbiological control of food evaluates the presence or absence of specific microbial groups and their evolution during storage. In particular, it is important to evaluate the spoilage microorganisms (bacterial Bacterial Total Mesophilic Aerobic) that provide interesting information on the state of hygiene and cleaning conditions adopted during processing and pathogenic microorganisms that define the safe use of a food. The evolution over time of spoilage microorganisms establishes the limits of edibility of the product.

Figure 2.5 shows the time stability limit within which the product retains the characteristics compatible with the marketing.

Predictive microbial growth studies can be used to predict the shelf life of products at any point from processing to purchase and provide useful

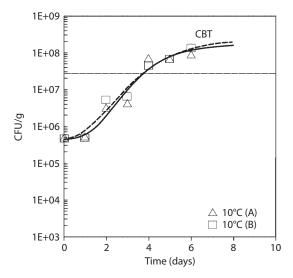


Figure 2.5 Curve of the microbial load of a product in function of time.

information in order to inhibit the growth of spoilage and pathogenic organisms.

Predictive food microbiology (PFM) is an emerging multidisciplinary area of food microbiology. Predictive microbiology is the integration of traditional microbiology knowledge and its objective is to develop mathematical modeling with an emphasis on modeling techniques, descriptions, classifications and their recent advances that describe the behavior of microorganisms under different environmental factors (physical, chemical, competitive) [11–13]. Predictive models allow the estimation of the shelf life of foods, isolate critical points in the production and distribution process and can give insight on how environmental variables affect the behavior of pathogenic or spoilage bacteria. The models used in predictive microbiology are developed from experimental work, usually conducted in laboratory media. These models are then extrapolated to foods.

# 2.4 Extending Shelf Life by Means of Food Packaging

There are many technologies that are "shelf life extending" and that maintain quality of foods. Among them the most widely used are packaging under vacuum, modified-atmosphere packaging (MAP), active and intelligent packaging.

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Vacuum packaging is used to increase the shelf life of food products. Here the product is placed in an air-tight pack, the air sucked out and the package sealed. By removing air from around the product, the levels of oxygen in the packaging are reduced, impeding the ability of oxygenbreathing microorganisms to grow and spoil the product. The lack of oxygen also reduces the amount of spoilage due to oxidation—the process that causes apples and bananas to turn brown, for example.

A certain amount of oxygen will remain, however, because it is not possible to create a total vacuum. Air contains around 21 per cent oxygen at normal atmospheric pressure—1000 millibar. As the air is withdrawn during the vacuum packaging process, the pressure inside the package is reduced.

The MAP process is certainly more versatile than vacuum packaging. Vacuum packaging consists solely of removing air. On the other hand, MAP can be tailored to the particular foodstuff, with different gases and different proportions of gas in the mixture used to give the maximum shelf life for the particular product and to retain the quality and appearance of the product. One area where MAP is better than vacuum packaging is in the presentation of the product. In vacuum packaging, as the pressure within the packaging is reduced the packaging material collapses and forms itself tightly around the product. For some products, such as fresh meat, this can distort the appearance of the product. Other products, such as shredded cheese, are not suitable for vacuum packaging because the pressure of the packaging material on the product would cause the product to deform and to lose important characteristics.

Another aspect in which the two processes differ is in the ease of quality control of the packaging process. In MAP packaging, air is flushed from the package and replaced with the gas mixture, making it possible to constantly monitor the gas content of the package during the packaging process. Once the package is sealed, any leakage of the modified atmosphere can be detected, enabling the integrity of the seal to be assured. For vacuum packaging, because there is no gas present in the package, leak testing is typically done through manual inspection, making quality control less straightforward.

Storage of foods in a modified gaseous atmosphere can maintain quality and extend product shelf life by slowing chemical and biochemical deteriorative reactions and by slowing or in some instances preventing the growth of spoilage organisms.

Modified atmosphere packaging (MAP) is defined as "the packaging of a perishable product in an atmosphere which has been modified so that its composition is other than that of air" [14]. Whereas controlled atmosphere storage involves maintaining a fixed concentration of gases surrounding the product by careful monitoring and addition of gases, the gaseous composition of fresh MAP foods is constantly changing due to chemical reactions and microbial activity. Gas exchange between the pack headspace and the external environment may also occur because of permeation across the package material.

Packing foods in a modified atmosphere can offer extended shelf life and improved product presentation in a convenient container, making the product more attractive to the retail customer. However, MAP cannot improve the quality of a poor quality food product. It is therefore essential that the food be of the highest quality prior to packing in order to optimize the benefits of modifying the pack atmosphere. Good hygiene practice and temperature control throughout the chill chain for perishable products are required to maintain the quality benefits and extended shelf life of MAP foods. The three main gases used in modified atmosphere packaging are  $O_2$ ,  $CO_2$  and  $N_2$ . The choice of gas is very dependent upon the food product being packed. Used singly or in combination, these gases are commonly used to balance safe shelf-life extension with optimal organoleptic properties of the food. Inert gases such as argon are in commercial use for products such as coffee and snack products; however, the literature on their application and benefits is limited.

The expression "functional packaging" generally refers to those packaging solutions in which is provided the use of a material, of a container or an accessory packing able to perform an additional function compared to traditional containment and generic protection product.

The term "active" refers to those packaging solutions that consistently and actively interact with the internal atmosphere of a package by varying the quantitative composition, or directly with the product it contains, through the release of useful substances to improve their quality or by the kidnapping of unwanted substances. The active packaging systems are developed with the goal of extending the duration of the food and increasing the period of time in which the food remains of high quality. The active packaging technologies include a number of actions with physical, chemical or biological weapons aimed at changing the interactions between the packaging and the product so as to obtain the desired result [15].

The most common active system recycles the oxygen from the packaging or the product and may even activate it through an external resource such as UV rays [16]. Active packaging is usually found in two types of systems; bags and pads that are inside the package and active ingredients that are embedded directly into the packaging material.

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The term "intelligent" indicates a packaging technique that involves the use of an indicator, internal or external to the package, able to objectively represent the history of the product and therefore its level of quality. Intelligent packaging can bring the conditions outside of the package, or directly measure the quality of the food inside the package. In order to measure the quality of a product inside the package there must be direct contact between the food and the quality marker.

In the end, an intelligent system could help the consumer in the decisionmaking process by extending the duration, enhancing security, improving quality, providing information and warning of potential problems.

Intelligent packaging belongs to the category of the time temperature indicator (TTI). The TTI is useful because it tells the consumer when the temperature of the food has been abused. If a food is exposed to a higher temperature than recommended, the quality of the food can deteriorate very quickly. A TTI can be placed on container ships or individual packaging label adhesive, and an irreversible change, such as a color change, will just indicate that there has been a change in conditions.

Another example of intelligent packaging is represented by the thermochromic inks that are sensitive to temperature and may change color accordingly. These inks can be printed on packaging and or labels in order to convey a message to the consumer based on the color of the ink that is seen. The thermochromic inks are becoming a popular technology for drinks [17]. The inks used, however, can be damaged by UV radiation and temperatures above 121°C, so the consumer cannot decide when to consume food.

These synthetic and schematic definitions hide an amplitude of innovation and technological complexity that is almost surprising. Materials are used very differently from the traditional ones or traditional ones are profoundly modified in various ways. In order to achieve the desired effect, materials take different forms and types (bags, films, accessory closures). The view of functional packaging solutions is very articulated and differentiated, and most importantly, truly innovative compared to the usual.

# 2.5 The Role of Packaging

In recent times food packaging has assumed an important role in food preservation having the following objectives:

• To meet the requirements of food safety for the protection of consumer health;

- To be an effective protection against chemical and microbiological contamination;
- To be a means to provide the consumer with information about the quality and the story of its content;
- To optimize shelf life.

Packaging is therefore one of the most important stages in the marketing of a product.

The utilized materials must be free of substances that could in any way interfere with the chemical level in packaged food, altering taste, shape or smell.

In this regard it is important that the link between packaging and shelf life also takes into consideration the fact that currently the consumer requires always higher food market standards of quality and safety; consequently, the entire chain of production dedicates much effort to optimizing all stages of preparation and marketing, with the mode of product packaging having a central role.

Shelf life means the period of time in which a food product retains, within acceptable levels, the chemical and physical composition, nutritional value, microflora, safety, health and hygiene, and the characteristics of taste, color, odor/aroma, and consistency. These parameters can be influenced by several factors, such as exposure to light, temperature, mechanical stress, microbial contamination, gases, humidity and packaging.

It is possible to distinguish between:

- *Primary shelf life:* Period of time during which a product, under specific conditions of packaging, storage and distribution, maintains hygienic, nutritional and/or sensory acceptable characteristics;
- Secondary shelf life: Period of time during which a product, under specific storage conditions, maintains its hygienic, nutritional and/or sensory acceptable characteristics after opening the package.

The relationship between primary and secondary shelf life is the extension of duration due to packaging and therefore the minimum shelf life that a product must have in order to remain competitive in the market.

The shelf life is determined mainly by marketing considerations related to consumer behavior and the distribution needs. It is always advisable to design the products and their packaging in order to reach or exceed the expected shelf life, but it is also desirable to avoid excessive protections (overpackaging) and unnecessary costs.

The packaging operation takes an "active" role in controlling the phenomena of decay, not a simple protection from degradation as it does in traditional packaging, or the "passive" role of the evacuation of the air from the package, but the ability to intervene in controlling certain degradative processes.

Food packaging is the process by which a food product is applied to physical protection, called packing, which prevents or minimizes the influence of the external environment.

The food packaging is of fundamental importance in reference to at least four aspects of the life of a food product industry: containment, storage, marketing and transportation.

- *Containment:* the packaging is essential to contain and support the amount of product that constitutes the unit of sale if the product is a liquid (milk) or other fluid (pudding) or powder (flour), or composed of small parts that need to be kept together (cookies) if it does not have a rigid structure (steak).
- *Storage:* packaging can be considered as a method of preservation, aimed at extending the life of the product for the purpose of marketing.

In the great majority of cases, suitable packaging is a subsidiary of a technique (freezing, dehydration, pasteurization, sterilization, etc.), making ineffective any alteration processes of the product; in these cases the packaging serves as a barrier to ensure the permanence of the virtuous situation obtained with the applied process.

- *Marketing:* the packaging determines the unit of sale (in addition to any subunit), includes all the necessary information for a correct identification by type of product, a knowledge of its physical characteristics and nutritional characteristics, methods of conservation and use of deadlines, the identification of the manufacturer and the seller, in addition to host images and striking colors for the purchase.
- *Transport:* the finished products in the warehouse/shipping industry production, as well as the incoming raw materials, must have a set-up that it can be managed (loading, unloading, stowage) with maximum efficiency; and the

final packaging, consisting of large units and regular forms, allows for the economical use of appropriate mechanical means (fork, ribbons, containers, etc.).

Packaging must contain the product, which means preventing leakage, or keeping together a multi-part product, e.g., a pack of soup sachets, or a number of different items brought together as one meal in a pack. Leakage is not only undesirable in that it almost certainly renders the product inedible, but it can also cause irrevocable and costly damage to neighboring packs and products.

Gradual leakage due to poor pack sealing can potentially cause more problems than catastrophic failure, especially if the problem goes unnoticed at the point of sale. By this time even if the product remains wholesome and fit for consumption, the weight may be below the legally allowed tolerance.

During its journey from source to final consumer, the product will be exposed to a number of different hazards, and packaging must provide physical protection against these hazards. The complexity and cost of modern food processing has meant a greater tendency to fewer and larger processing and packaging operations, bringing with it greater journey distances and multiple handlings for the final packed product.

Damage can result from mechanical and environmental hazards throughout this supply chain. Products can be jolted and subjected to vibration on vehicles and compressive loads during stacking in warehouses, all of which can potentially damage both the product and the pack. Owing to external forces, damage effects include breakage of fragile products such as biscuits and weakening of pack closure systems such as heat seals and screw caps, thereby destroying the preservation function. Environmental hazards include exposure to light and to high and low temperatures and humidity levels, dust and dirt, and insect and rodent infestation. Human hazards must not be forgotten here. The threat of tampering, whether malicious or just curious, has led to manufacturers having to consider the tamper evidence of their packed products and, where necessary, incorporating additional devices to deter tampering.

Another important role of packaging is to provide a convenient way of handling the product, all the way from the packaging line to final consumption and pack disposal. Good packaging line performance consistently achieves correctly formed and sealed packs, which are critical for maintaining the preservation function with which this chapter is concerned. Poorly sealed packs mean vastly reduced shelf life. Good performance in what are usually very busy storage and handling environments means that packaging must provide ease of movement of the goods, with maximum efficiency and minimum effort.

Convenience in product use is one of the major benefits of packaging, and innovative solutions can provide major points of difference from one product to another. Convenience features abound in modern food packaging. The bottle of oil which allows for careful dispensing of the product is superior to that which permits the product to pour out uncontrollably. Ready-prepared meals which allow us to take the pack directly from the freezer and put it in the microwave or conventional oven save time and reduce washing up. Most importantly for today's busy consumers, ease of opening and, if relevant, reclosing are essential considerations. If the contents of the pack cannot be removed without causing frustration to the person opening it, he/she will at the very least register a silent protest by purchasing a different type of pack in the future. If attempts to open the pack result in damage to the consumer, the protest may not be silent and may be a very costly and image-damaging lawsuit against the brand owner.

# 2.6 Innovative Polymers for Food Packaging Applications

The market demands packaging of food products characterized by a high barrier to oxygen and water vapor (critical for the proper preservation of perishable packaged products) and high quality, able to meet the expectations of consumers. The packaging, once considered only useful to protect the product, has become an important tool for marketing, communication and sales. Through the packaging useful information comes to the consumer for the proper use of the item purchased.

The materials used to produce packaging and articles intended for food contact constitute a family which is not very large, but heterogeneous with different characteristics. The knowledge of the properties and performance of materials that are used to make food packaging is of paramount importance to make a correct choice of the type of protection for the product.

The choice of material, however, is of paramount importance, for mistakes made in the selection of the material can have very serious repercussions in economic terms or in terms of the quality of the packaged product. And therefore it is absolutely appropriate to have adequate knowledge of the properties of solids, which can guide the evaluation or of the material to be used for a specific type of packaging. Innovative and intelligent packaging constitutes a branch of such a sector that is truly innovative and offers exciting opportunities for the safety, quality and affordability of food.

Many active and intelligent packagings are commercially available in the United States. Some experts believe that the next technological development of packaging will include nanotechnology that will add new components such as antimicrobials and gas scavengers in packaging films.

The development of electronic devices can be made cheaply and will lead in the direction of innovative active and intelligent packaging. As society continues to evolve, consumer expectations continue to advance. The use of active and intelligent packaging will become more and more popular now that the technologies finding space in the market are becoming more common. Perhaps active and intelligent packaging will completely replace traditional packaging. And, as Paul Gander states in *Food and Manufacture*, "the trend is towards less use of packaging, but more interactive." If 2020 sees packaging that literally walks down from the shelves, is another matter [16].

Moreover, nowadays a wide range of polymer-based nanomaterials are used in applications which involve contact with food or beverages: particularly in foodstuff packaging applications, utensils, kitchenware and in processing equipment in food factories and other places where food is handled in large quantities [18].

The use of nanotechnology in food packaging is expected to grow rapidly in the next years, though its application in food packaging is at a developmental stage. Simple conventional packing is to be replaced by multifunctional intelligent packaging methods to improve the food quality thanks to the application of nanotechnology in this field. New packaging solutions will increasingly focus on food safety by controlling microbial growth, delaying oxidation, improving tamper visibility and convenience [19].

Applications in this area already support the development of improved taste, color, flavor, texture and consistency of foodstuffs, increased absorption and bioavailability of nutrients and health supplements, new food packaging materials with improved mechanical, barrier and antimicrobial properties, and nanosensors for traceability and monitoring the condition of food during transport and storage. Particularly the latter are very interesting, since, for example, with embedded nanosensors in the packaging, consumers will be able to "read" the food inside. Moreover sensors can warn us before the food goes rotten or can inform us of the exact nutrition status contained in the contents.

Some reported examples of nanosensors applied to the food packaging sector are as follows:

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- Scientists at the University of Connecticut [20] are working on nanoparticle films and other packaging with embedded sensors that will detect food pathogens. Called "electronic tongue" technology, the sensors can detect substances in parts per trillion and would trigger a color change in the packaging to alert the consumer if a food has become contaminated or if it has begun to spoil.
- Researchers in the Netherlands [21] are going one step further to develop intelligent packaging that will release a preservative if the food within begins to spoil. This "release on command" preservative packaging is operated by means of a bio-switch developed through nanotechnology.
- Developing small sensors to detect foodborne pathogens will not just extend the reach of industrial agriculture and large-scale food processing. In the view of the US military, it is a national security priority. With present technologies, testing for microbial food contamination takes two to seven days, and the sensors that have been developed to date are too big to be transported easily.
- Several groups of researchers in the US are developing biosensors that can detect pathogens quickly and easily, reasoning that "super-sensors" would play a crucial role in the event of a terrorist attack on the food supply. With USDA and National Science Foundation funding, researchers at Purdue University [16] are working to produce a hand-held sensor capable of detecting specific bacteria instantaneously from any sample.

In the frame of nanostructured materials for food and beverage packaging applications, in this chapter we have reported the results of our work concerning the preparation and characterization of two new polymerbased nanocomposite systems that can be used as food packaging materials. Particularly the results concerning the following systems are illustrated: isotactic polypropylene (iPP) filled with CaCO<sub>3</sub> nanoparticles and polycaprolactone (PCL) filled with SiO<sub>3</sub> nanoparticles.

Some studies of innovative polymers for food shelf-life extension are discussed below.

## 2.6.1 Biopolymer-Based Nanocomposites for Vegetable Packaging Applications

The growing interest in the environmental impact of discarded plastics has stimulated research in the development of plastics that degrade more rapidly in the environment, leading to their complete mineralization or bioas-similation [22–25]. Thus, there is a considerable interest in replacing some or all of the traditional non-biodegradable polymers, especially in short life-time applications such as packaging, or when their recycling is difficult and/or not economical.

Some of the natural polymers (polyhydroxybutyrate (PHB) and its copolymers) and aliphatic polyesters (polycaprolactone, polylactic acid) are biodegradable, but they are expensive compared with petroleum-based plastics, and this high cost prevents their wider commercial usage, leading them to find applications only in niche sectors [26–32]. Among the biomaterials now available in the market, those derived from renewable resources such as starch-based products are the most widespread and economic [33–37]. Some examples are Mater-Bi from Novamont, Italy, and BIOPAR from Biop, Germany. The starch is normally blended with biodegradable aliphatic polyesters such as Ecoflex from BASF, Germany, or Bionolle from Showa Highpolymer, Japan [38,39].

Unfortunately the starch presents some drawbacks such as its hydrophilic behavior (poor moisture barrier) and mechanical properties that are weaker than the conventional non-biodegradable plastic films used in the food packaging industry. The realization of thermoplastic starch (TPS)based nanocomposites by dispersing functionalized layered silicates (clay minerals) via melt processing techniques overcomes these problems. Nanocomposite films were realized by casting, using thermoplastic potato starch supplied by Avebe, Netherlands, and an organo-clay (montmorillonite, sample code 12) with a cation exchange capacity (CEC) of 128 meq/100 g, supplied by Laviosa (Livorno, Italy).

Tensile properties such as those measured by Young's modulus, strength at break, and strain at break were calculated from the experimental stressstrain curves recorded on all prepared nanocomposite films. The mechanical test was carried out on samples stored at different relative moisture contents in order to simulate different storage conditions.

The mechanical parameters are displayed in Table 2.4. As shown, the TPS/C sample is characterized by the highest Young's modulus and stress at break with respect to the other materials, thus underling an effective clay reinforcing effect. The addition of biodegradable polyester to the mixture (TPS/PE and TPS/PE/C samples) decreases the Young's modulus,

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Sample codes	wt% Clay	Young modulus (MPa)	Strength at break (MPa)	Strain at break (%)
Materials cond	itioned at 159	% relative humidity	,	
TPS	0	979	19	3
TPS/C	4	1135	22	4
TPS/PE	0	682	7.5	2
TPS/PE/C	4	374	7.8	38
Materials cond	itioned at 60°	% relative humidity	r	
TPS	0	610	9	9
TPS/C	4	830	10	2
TPS/PE	0	150	3.6	21
TPS/PE/C	4	137	4.7	58

 Table 2.4
 Mechanical properties of the prepared materials.

increasing the strain at break. These results agree with the morphological and structural analyses. In fact, it was underlined that the TPS/C sample is characterized by a good intercalation of the starch phase into the clay layers, while a polyester phase separation was observed in the TPS/PE and TPS/PE/C samples.

Finally, the conformity of the prepared starch/clay nanocomposite films to the actual regulations and European directives on biodegradable materials was examined, in terms of heavy metal and other toxic and hazardous substance content and migration, in particular for packaging of vegetables. The EC guidelines on food contact materials require that they shall be safe and shall not transfer their components into the foodstuff in unacceptable quantities. In fact, plastic materials are not inert and when direct contact between the packaged product and the plastic container occurs, there can be migration of substances into the product. The amount of any component that migrates into food depends on its concentration in the polymer and its solubility, as well as on temperature, mechanical stresses, and contact time. It is extremely difficult to measure the migration directly into food, as most foodstuffs have a complicated composition. For this reason, the migration behavior of the plastic material is more easily measured by using so-called food simulants such as ethanol, water, etc. [40]. The extractability of a compound from the plastic can be determined by placing the plastic in contact with the food or food simulant under defined conditions of temperature and time in a static or dynamic mode. An appropriate analytical technique

is then employed to determine the amount of compound present in the food/stimulant, and hence the degree of migration can be calculated. The overall interaction of plastic packaging materials with foodstuffs is best described by global migration, which is the sum of all the specific migrations of plastic constituents and foodstuffs [41,42].

Two types of migration limits have been established in the area of plastic materials: an overall migration limit (OML) of 60 mg/kg (of foodstuff or food simulants) and a specific migration limit (SML), which applies to individual authorized substances and is fixed on the basis of toxicological considerations.

Energy dispersive X-ray spectroscopy (EDAX) analysis showed a heavy metal content well below the permitted limits in all the TPS-based samples; but the eventual metal migration during contact with a selected foodstuff (lettuce) was measured anyway. The results of specific migration analysis relative to Fe, Mg, and Si are shown in Table 2.5, where it can be seen that the contact of the different films with lettuce did not produce a significant increase of Fe and Mg in the vegetables. The higher Si content observed can easily be attributed to the clay nanoparticles.

Finally, a test for measuring the overall migration after contact with a common vegetable simulant (water) on the starch-based films was also performed. The samples were immersed in distilled water at 40°C for 10 days. The test was performed on films after drying under vacuum and storage in a plastic bag and showed negligible overall migration.

In conclusion, biodegradable starch/clay nanocomposite, prepared by homogeneously dispersing montmorillonite nanoparticles via polymer melt processing techniques, can be applied successfully to vegetable packaging, as for the mechanical properties as for the conformity of starch/ clay nanocomposite films with actual regulations and European directives

Sample	Fe	Mg	Si
Lettuce	2.2	45.7	0.28
TPS	2.4	14.8	1.3
TPS/C	3.7	77.1	1.9
TPS/PE	1.4	31.9	1.3
TPS/PE/C	2.1	43.1	1.6

**Table 2.5** Fe, Mg, and Si content in vegetables before and after contact with nanocomposite films ( $mg \times 100$  g).

on biodegradable materials, demonstrating that these materials can be utilized in the food packaging sector owing to their low overall migration limit.

### 2.6.2 Innovative Polyamide-Based Packaging of Fresh Meat

Nowadays the market distribution system of fresh meats (i.e., larger supermarkets and hypermarkets) requires a product that is able to maintain its original sensory and nutritional characteristics as long as possible [43–45]. The most important method to achieve this goal is represented by the use of the so-called cold chain, which means that the refrigeration and freeze is properly applied to inhibit the development of microbial flora originated from the meat deterioration and microbiological decay [46]. Although a natural antibacterial property exists in meals, the prevention of microbial contamination remains an efficient way to limit its hygienic/sanitary and sensory damages. Some scrupulous hygienic norms during the slaughtering, transformation, and commercialization processes are not enough to prevent meat contamination.

In fact, several studies have suggested that some methodologies for the conservation of fresh and transformed meats [47–49] by using (1) preservatives; (2) bacterial cultivations with a specific antagonistic activity generating some specific metabolites (i.e., lactic acid and bacteriocins) [50]; and (3) gases, such as  $O_2$ ,  $N_2$ ,  $CO_2$ , or their gaseous mixtures; are able to hinder or delay the microbial increase [51]. Innovative polyamide-6-based polymer films were investigated with migration tests by using some fat simulating substances [52] and the migration ability (particle cession) from the package to the produce and vice versa was determined to ascertain their suitability in the alimentary field [53–55]. The existence of the main bacteria groups and the pH values measured before and after the conservation of the meats are reported in Figures 2.6–2.8 for various polymer films. Figure 2.6 shows the total microbial concentration detected in the fresh and stored meats of the packages at 4°C for 6 days.

The bacterial concentrations were found larger in both the meat stored in polyethylene and the pure nylon films than those detected in the fresh meat conserved in Ny/EVOH and Ny/EVOH/COOH polymer films. In Figure 2.7, the populations of the main microbial groups constituting the natural microflora and contaminants of the meat, such as lactic acid bacteria, Micrococcaceae, Enterococcus spp., yeast and molds, enterobacteria, and fecal choliforms, were reported before and after the packaging.

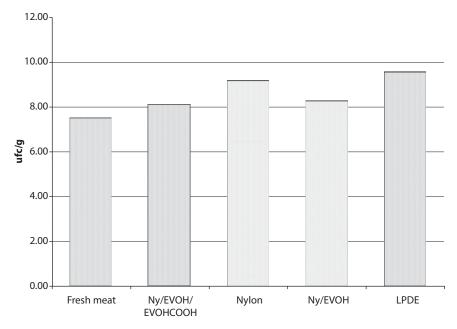


Figure 2.6 Development of microflora in fresh and packaged meat.

This figure puts proves that the film made by the ternary blend is able to limit the increase of yeasts, Micrococcaceae, and the fecal choliforms, while the pure nylon sample is not able to perform any action of slowing down or inhibition of the existing bacterial flora, out of a slight reduction in the increase of Enterococcus spp. and the lactic acid bacteria. An intermediate behavior was observed for the meats stored in the Ny/EVOH blend film. On the contrary, the meats stored in the polyethylene film show an increase of all microbial groups up to 10<sup>9</sup> ufc/g, thus promoting the complete deterioration of the product. The values of pH measured on the meats in various packages were reported in Figure 2.8.

These data were collected before and after the conservation for a period of 6 days at 4°C. The pH of the meats stored in the Ny/EVOH/COOH film is lower compared with those of the fresh meats. In contrast, the pronounced pH values in the meats stored in the nylon and polyethylene films clearly indicate the beginning of the deterioration processes. The meats in the binary Ny/EVOH alloy film show an intermediate pH value with respect to other polymer materials based on Ny6 and Ny/EVOH/COOH films. The measured decrease of pH values in the stored meats in the Ny/ EVOH/COOH film can be correlated with the increase of the lactic acid bacteria [51]. Therefore, these results suggest that the recorded pH values

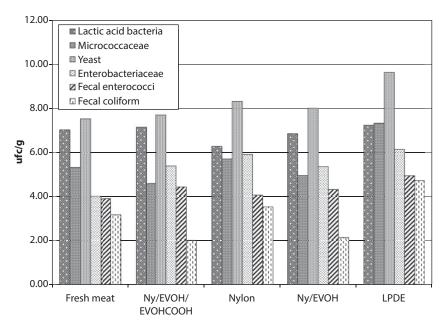


Figure 2.7 Development of spoilage microorganisms in fresh and preserved meat.

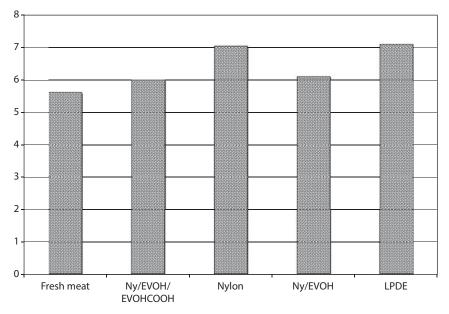


Figure 2.8 pH values of fresh and packaged meat.

are in agreement with the trend of the mesophilic microbial population, as shown in Figure 2.8. These results also indicate that the composition of the ternary blend, imparting the best oxygen barrier [52], shows an inhibition effect toward the development of the natural microflora. The measured surveying of twofold activity suggests that the inhibition with respect to aerobic is dependent on the microorganisms and some microaerophilics, such as Micrococcaceae, yeasts, enterobacteria, and fecal choliforms.

This result can explain the increase of the lactic acid bacteria, whose antagonistic effect toward the putrescent microflora is well documented [52].

The deep-red color of the meat is a parameter of paramount importance, because it is chosen by the end consumer as a freshness and quality index [54]. In fact, the chromatic changes with respect to the standard initial color are interpreted as signs of bad conservation. The pigments of the meats are mainly constituted by the myoglobin, and in a minor content by the hemoglobin, cytochromes, and flavine. The myoglobin is a protein formed from both a globulinic and a prosthetic, not polypeptidic, component, defined as eme, showing a center directly linked to an iron cation. The eme shows a reductive or oxidative behavior depending on its ability to bind an oxygen atom, in this way determining the various chemical properties of the myoglobin. In a reduced form, iron (II) binds to an oxygen molecule imparting to meat a deep-red color (oxymyoglobin). On the contrary, iron (III) loses its ability to bind oxygen in the oxidized form and the meat becomes purple-brownish in color (metamyoglobin). We tried to determine color variations between fresh and stored meats by using the UV-Vis spectrophotometric measurements to follow the absorbance changes related to the concentration ratios between the oxymyoglobin and metamyoglobin contents. The absorbances are reported in Figure 2.9 at three different wavelengths, 410, 560, and 580 nm, for some different meats.

The absorbance at 410 nm (corresponding to the myoglobin of fresh meat [55]) remains undoubtedly high when the meats are conserved in the ternary blend film packaging for 6 days. In contrast, in the same sample, the absorbances at 560 and 580 nm (corresponding to the oxidized state of myoglobin) are less pronounced than those stored in the binary blend and LDPE films [56]. These results are in agreement with the abovementioned microbiological tests in which the ternary blend shows the best performances toward inhibition of the meat contamination, because the absorbance found at 410 nm is more pronounced than those films derived from the binary blend and pure polymer film.

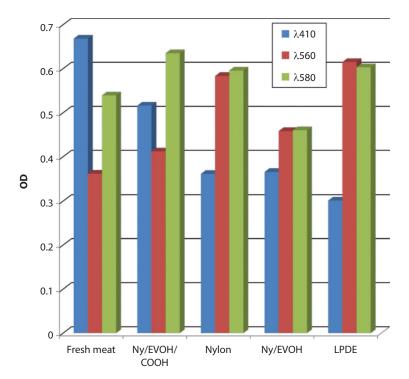


Figure 2.9 UV absorbances as function of preservation time.

The innovative film based on Ny/EVOH/modified EVOH ternary blend film, in comparison with the pure Nylon 6 and a binary Ny/EVOH blend film, shows a good oxygen barrier inhibiting the oxidation of commercially available fresh minced meat. The same behavior was observed for the same investigated polymer materials tested with some fat-containing simulating foods. Under the same testing conditions, the enzymatic and fermentative processes, due to the meat deterioration, are simultaneously decreased when a ternary blend film is used.

These inhibition effects were attributed to the blend component intimate dispersion in achieving an improvement of the EVOH atmospheric oxygen barrier of the polymer film matrix. The retention of the daylight transmittance and color of the tested polymer films maintained an intimate contact with the minced meat, which shows the absence of the contamination and swelling phenomena under the packaging conditions.

### 2.6.3 Innovative Packaging for Minimally Processed Fruits

Minimally processed (MP) fruits are spreading in answer to the increasing demand for easy and fast products with fresh-like quality. The increasing use of foods ready for consumption is due to their ability to satisfy new food habits following lifestyle changes. These products maintain a quality similar to that of fresh products. In fact, washing, sorting, peeling and cutting of fruits and vegetables are completely automated in order to limit manipulations and to guarantee the hygienic characteristics of the product [57].

The rapid darkening of many fruits is a serious problem during minimal processing operations. Appropriate steps must be taken during fruit processing against oxidation phenomena. Browning damages the appearance, organoleptic properties and nutritional quality of fruits [58]. Generally, the market for MP products belongs to vegetables, but recently much attention has been turned to the possibility of also manufacturing fresh fruits [59]. Truly, packaged MP fruits are already available, but they represent niche products having high production costs and needing the cold chain for their commercialization.

The greater part of the literature on ready-to-eat fruits and vegetables is based on the use of modified atmospheres [60–64], where the air is replaced by a gas mixture, or on the use of controlled atmospheres [65], where the proportions of the gases are kept under control during the whole storage period. Obviously, these methodologies increase production costs.

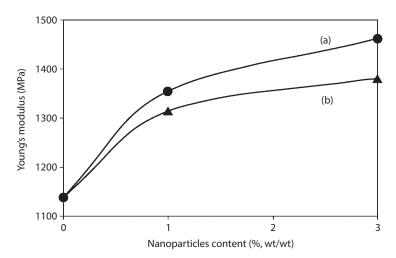
Among several thermoplastics, polyolefins are the most used plastic materials in the food packaging sector [66]. Isotactic polypropylene (iPP) films hold a prominent position in this field because of their transparency, brilliance, low specific weight and chemical inertness. Unfortunately, polypropylene, like other polyolefins, is characterized by low barrier properties, which results in poor protection of the packaged food [67]. One of the most useful methods to improve polypropylene drawbacks is to add a second component such as a polymer in blend or in multilayers, fillers, etc. [68–70].

Nowadays, polypropylene-based nanocomposites are a major industry challenge because they represent the route to substantially increasing the mechanical and physical properties of such a widely used thermoplastic commodity [71–75]. Nanocomposites can achieve same or higher properties with only a low percentage of filler (1–5 wt%), thus preserving polymer processability and recycling. The key factors in the preparation of high performance nanomaterials are to obtain a fine and homogeneous dispersion of the nanoparticles and to promote strong interfacial adhesion between

matrix and nanofillers. The iPP-based nanocomposites for potential use in the packaging of MP foods such as apple slices were prepared and characterized. For this purpose, innovative modified calcium carbonate (CaCO<sub>3</sub>) nanoparticles, characterized by a spherical and elongated shape, were tested. In particular, CaCO<sub>3</sub> nanoparticles of spherical and elongated shape, coated with iPP-maleic anhydride and characterized by different crystal modification were used for nanoreinforcing of iPP polymeric matrix. An iPP-g-MA coating agent was selected because of its similar chemical nature to that of the polymeric matrix that could ensure strong coated nanoparticles/iPP interactions, thus allowing good matrix/nanofillers interfacial adhesion.

The mechanical results reported in Figure 2.10 suggest that there is a significant influence of the nanoparticle shape on the extent of the mechanical improvement. Therefore, the different specific surface area of the nanoparticles in contact with the polymer matrix was the main factor influencing the improvement of the final properties.

Generally, the addition of inorganic fillers into a polymer could affect the gas diffusion mechanism through the material because of the different permeability properties of the matrix and the foreign particles. This phenomenon is particularly stressed when a filler of nanometric size is dispersed into the polymeric matrix because of the high specific surface of nanoparticles responsible for the wide contact area between the phases.

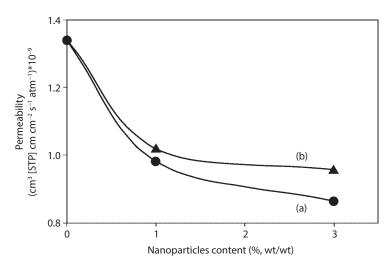


**Figure 2.10** Trend of the Young's modulus as a function of amount and shape of the  $CaCO_3$  nanoparticles: (a) iPP/S-CaCO<sub>3</sub> nanocomposites; (b) iPP/E-CaCO<sub>3</sub> nanocomposites.

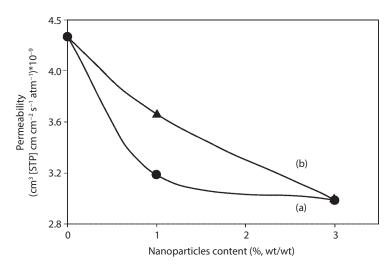
Moreover, the tortuous path that diffusing molecules have to bypass because of the presence of nanoparticles is an additional phenomenon that must be taken into account to study the nanocomposite permeability property [76–79]. As can be observed, nanoparticles (Figures 2.11 and 2.12) significantly influenced iPP barrier properties either to oxygen or to carbon dioxide, reducing both the coefficient permeability values by up to about 30% as a function of the amount of nanoparticles. Furthermore, spherical nanoparticles were responsible for a slightly more pronounced decrease of permeability with respect to that obtained by the addition of elongated nanoparticles.

Migration tests showed that all the nanocomposite films undergo migration values that are comparable, within the experimental errors, with those recorded for neat iPP, independently from the amount of nanoparticles (1% and 3% w/w) and from their shape. Therefore, all the tested films are suitable for food packaging applications because the release of nanoparticles or other substances is negligible and, in any case, lower than the allowed limit of 10 mg/dm<sup>2</sup> [78]. In Figure 2.13 the total mesophilic microflora enumerated on apples stored for 5 and 10 days at 4°C is reported.

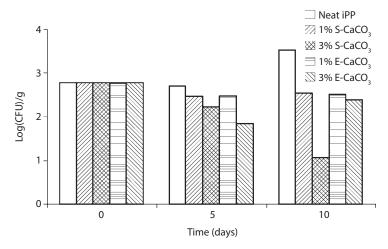
As can be observed, the total mesophilic microflora increases as a function of storage time in the case of apples packaged in neat iPP films. Concerning iPP-based nanocomposites,  $CaCO_3$  nanoparticles caused a decrease of this parameter with respect to that recorded at starting



**Figure 2.11** Variation of the oxygen permeability as a function of amount and shape of the  $CaCO_3$  nanoparticles: (a) iPP/S-CaCO<sub>3</sub> nanocomposites; (b) iPP/E-CaCO<sub>3</sub> nanocomposites.



**Figure 2.12** Variation of the carbon dioxide permeability as a function of amount and shape of the CaCO<sub>3</sub> nanoparticles: (a) iPP/S-CaCO<sub>3</sub> nanocomposites; (b) iPP/E-CaCO<sub>3</sub> nanocomposites.



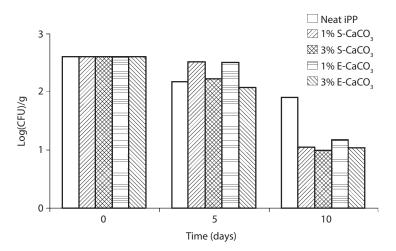
**Figure 2.13** Total microbial counts on apple slices at time zero (t0) and after 5 and 10 days of storage at 4°C in different packaging materials.

time (t0), thus preventing the growth of natural microflora. Moreover, the microorganism growth seems to be influenced by the shape and the amount of nanoparticles. In fact,  $S-CaCO_3$  nanoparticles led to a reduction of microflora of up to 65% as a function of time and nanoparticle content. On the other hand, the presence of elongated nanoparticles allows a slightly larger microorganism growth decrease than that observed with

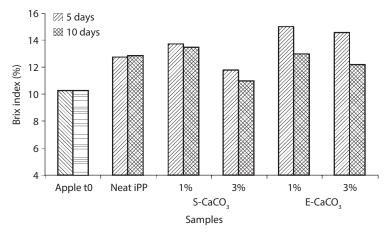
spherical nanoparticles after the first 5 days of storage, while a successive increase was recorded in the next 5 days. Nevertheless, this microorganism growth increase assures smaller values than those recorded on apples at t0. These findings underline a strict correlation between nanocomposite barrier properties and total mesophilic microflora enumerated during storage time. In fact, as described above, spherical nanoparticles were responsible for a more pronounced improvement of barrier to oxygen in comparison with that obtained with E-CaCO<sub>3</sub>. This enhanced property can justify the reduction effect of CaCO<sub>3</sub> nanoparticles on microorganism growth, particularly marked in the case of S-CaCO<sub>2</sub>.

In Figure 2.14, mold population on apples as a function of storage time and nanoparticle shape and amount is reported. This microbiological analysis showed a reduction of mold growth due to the presence of nanoparticles attributable, also in this case, to the increase of barrier to oxygen recorded for nanocomposites. In Figure 2.15, Brix index values are reported. As it is shown, during the first 5 days, a slight increase of Brix index values was recorded for apples packed both in neat iPP and in iPP-based nanocomposite films. In the next 5 days, Brix values decreased for apples packed in nanocomposite films, consistent with what has been reported in the literature. On the contrary, concerning iPP films, Brix values remained almost unchanged during the whole storage period.

Moreover, the most interesting finding is that apples stored in nanocomposite films containing 3% by weight of S-CaCO<sub>3</sub> show the lowest Brix index values. This result could be attributed to better barrier properties of



**Figure 2.14** Mold counted on apple slices at time zero (t0) and after 5 and 10 days of storage at 4°C in different packaging materials.

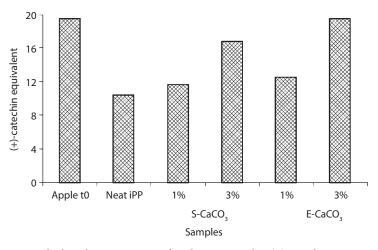


**Figure 2.15** Brix indices measured on apple slices at time zero (t0) and after 5 and 10 days of storage at 4°C in different packaging materials.

this nanocomposite towards gases, and possibly also to ethylene naturally developed during apple maturation, which, if retained in the packaging, facilitates maturation [79]. It is well known that determination of the polyphenol concentration, here expressed as ( + )-catechin, indicates oxidation phenomena occurring on the fruit. In particular, a more significant oxidative effect corresponds to a drastic decrease of the catechin value.

The ( + )-catechin concentration, after 5 days of apple storage, as a function of nanoparticle amount and shape is reported in Figure 2.16. This value was drastically reduced in apples packed in iPP films and in nano-composite films containing 1% by weight of nanoparticles. In the case of iPP-based nanocomposites containing 3% by weight of  $CaCO_3$ , polyphenol concentration values almost similar to that of fresh apples were recorded. Moreover, the nanoparticle shape did not seem to influence this value.

These results suggest that the presence of nanoparticles decreases apple oxidation phenomena, in particular at the highest loading of nanoparticles, with respect to that obtained by apple storage in iPP films. The iPP-based nanocomposites filled with CaCO<sub>3</sub> nanoparticles were prepared and characterized. Moreover, contact test measurements have shown that iPP/CaCO<sub>3</sub> nanofiller films satisfy the fixed limit of global migration of 60 mg/kg required for plastic materials. Usual parameters used to determine the food shelf life (microbiological analysis, Brix indices and polyphenol content) have demonstrated that iPP-based nanocomposites are able to guarantee the integrity of apple slices for up to 10 days.



**Figure 2.16** Polyphenol concentration of apples, expressed as (+)-catechin, measured at time zero and after 10 days of storage in neat iPP and in iPP-based nanocomposite films.

## 2.6.4 Natural Polysaccharides-Based Gels for Dairy Food Preservation

The real water buffalo mozzarella cheese (WBM) suffers a limited shelf life, and today many researchers focus on the development of new methodologies and innovative materials that increase the shelf life of foods, without impacting on their quality (so-called mild technologies).

The shelf life of mozzarella is strictly linked to the type of raw material used (not pasteurized milk) and to the technology of processing. The product obtained from unpasteurized milk and natural whey can be stored, immersed in its mother solution, for 3–4 days at a temperature between 4–10°C with no loss of its characteristics (translucent external skin, white color, soft and elastic curd, peculiar taste of fresh milk and wildness aroma) [80]. Beyond such period, the external skin peels off while the shred loses consistency and becomes buttery following the destruction of the overlapping shells structure obtained during high temperature stretching. Only industrial products, obtained with pasteurized milk and selected starter, can maintain a prolonged shelf life of up to 20 days, but the taste is absolutely unsatisfactory when compared with traditional artisan mozzarella.

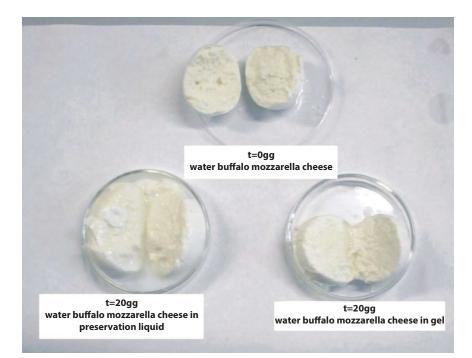
The development and realization of innovative packaging systems for mozzarella have been able to guarantee a prolonged shelf life of at least 15 days for traditional mozzarella, with no influence on the production methodology and no influence on the taste, mechanical properties and nutritional properties of the product. The basis of the innovation is first of all related to the choice of material: mixtures of biodegradable and biocompatible polymers belonging to well-known families of natural polysaccharides already approved for use in the agro-food industry. Such biopolymers represent the widest fraction of organic matter present on our planet, just to mention the most relevant representatives, cellulose, starch, chitin that are produced yearly in amounts of billions of tons. It is obviously more relevant in view of understanding the scientific and technological relevance of polysaccharides to underline the fact that very often they are constituted of highly stereoregular macromolecules, and are hydrophilic, reactive and also able to exhibit biological "intelligence" similar to that of the more celebrated biopolymers such as proteins and nucleic acids. As a consequence, many polysaccharides, being available in enormous amounts and with a wide range of chemical and physical behavior, either in bulk, in solution or in gel state, represent an unsubstitutable commodity.

Figure 2.17 shows the evolution of microflora isolated from water buffalo mozzarella cheese stored in preservation liquid (M) and in innovative gel (MA).

Water buffalo mozzarella cheese was stored, after packaging, at room temperature for 5 days (Figure 2.18) to evaluate the effects of temperature and media composition on natural microbial growth. Counts of the different groups of microorganisms, isolated from the water buffalo mozzarella cheese before packaging (samples M and MA), were included in the range 6 and 2 log10 ufc/g. Besides, there was an increase of 3 log10 ufc/g for total mesophilic microflora, lactic acid bacteria, and enterococci; while for yeasts, total and fecal coliforms there was a few increase. Thus the preservation of water buffalo mozzarella cheese at room temperature, promoting an increase of natural microflora, was not advised.

Figure 2.19 illustrates the counts of natural microflora isolated from the samples stored at 4°C for 5, 10 and 15 days. In the water buffalo mozzarella cheese stored in preservation liquid, total mesophilic microflora and lactic acid bacteria showed a higher increase than that stored in sperimental gel. Instead, enterococci flora revealed a different ability of growth in the samples (M and MA); in particular they were not able to grow in gel. The innovative gels based on natural polysaccharides used in this work had the peculiar characteristic to establish an unfavorable habitat for growth of natural microflora, above all enterococci flora.

At the beginning of tests and at regular intervals pH was measured on both cheeses. The values are reported in Table 2.6. In general, we noticed, in the case of the liquid medium, a trend of pH from more acidic to more alkaline values in 20 days (from 4.28 up to 5.00). The cheese stored in such

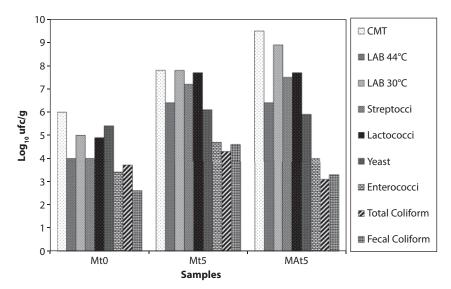


**Figure 2.17** Micrograph of water buffalo mozzarella cheese at time 0 and stored in preservation liquid and innovative gel for 20 days at 4°C.

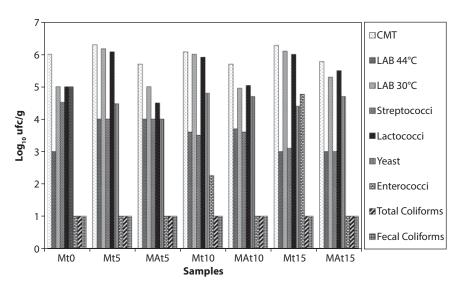
liquid showed a slight increase of pH from t0 (5.25) to t10 (5.42), while the values recorded at a later time are lower (at t20 the value reaches 5.02).

For the gel-stored cheese, the variations of pH were more regular, increasing regularly from t0 to t20 (from 5.25 to 5.60). The changes in pH during storage seems to be closely related to the structure of mozzarella, as reported in literature [81,82]. In many works a correlation is drawn between pH, calcium content and proteolysis of the mozzarella [83,84]. In general, a pH reduction increases the ratio between soluble calcium over colloidal calcium, which in turn would increase the degree of hydration of casein [85] and reduce its aggregation state, which in turn increases the susceptibility of casein to hydrolysis [86]. In the gel-stored mozzarella, on the contrary, all pH values are less different from the initial values and they vary, moreover, in an opposite direction, i.e., they go towards more alkaline values.

In order to study the protein fraction included in Mozzarella cheese the descriptive electrophoretic techniques currently used for monitoring casein hydrolysis in cheese [87] were used. In Figure 2.20 the isoelectric



**Figure 2.18** Microbial counts of water buffalo mozzarella cheese at time zero and stored at room temperature for 5 days: M = water buffalo mozzarella cheese stored in preservation liquid; MA = water buffalo mozzarella cheese stored in innovative gel; CMT = total mesophilic microflora; LAB = lactic acid bacteria.



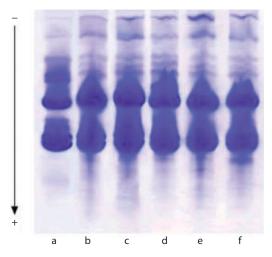
**Figure 2.19** Microbial counts of water buffalo mozzarella cheese at d 0 and stored at 4°C for 5, 10 and 15 days: M = water buffalo mozzarella cheese stored in preservation liquid; MA = water buffalo mozzarella cheese stored in innovative gel; CMT = total mesophilic microfiora; LAB = lactic acid bacteria.

**Table 2.6** pH of mozzarella cheese and storage media as measured at differenttimes.

Time (d)	Mozzarella <sup>1</sup>		Preservation liquid	Gel
	М	MA		
0	5.25	5.25	4.28	7.23
5	5.31	5.35	4.80	4.47
10	5.42	5.58	4.85	5.28
20	5.02	5.60	5.00	5.66

<sup>1</sup> M = Water buffalo Mozzarella cheese stored in preservation liquid;

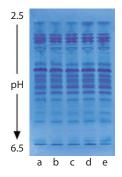
MA = Water buffalo Mozzarella cheese stored in innovative gels.



**Figure 2.20** Disc-P AGE analysis of the whole protein fraction from water buffalo mozzarella cheese samples stored at 8°C in gel (lane c) or in its own liquid (lane d) for 15 d, and in gel (lane e) or in its own liquid (lane f) for 44 d. The electrophoretic profiles of a freshly produced cheese sample and of a water buffalo whole casein sample, kept at  $-20^{\circ}$ C until the analysis, are reported in lanes a and b, respectively.

focusing profiles of the proteins extracted from samples of the same lot of water buffalo mozzarella cheese after a storage at 8°C in its preservation liquid (lane b) or in gel (lane c) for 15 days and in its preservation liquid (lane d) or in gel (lane e) for 44 days are reported and compared with the electrophoretic profile of proteins from a freshly produced cheese sample, kept at  $-20^{\circ}$ C until the analysis (lane a).

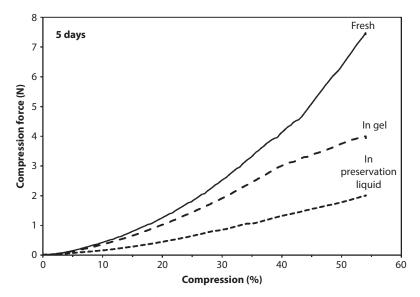
Disc-PAGE analysis of the whole protein fraction from the same mozzarella cheese samples analyzed in Figure 2.21 is shown in Figure 2.20.



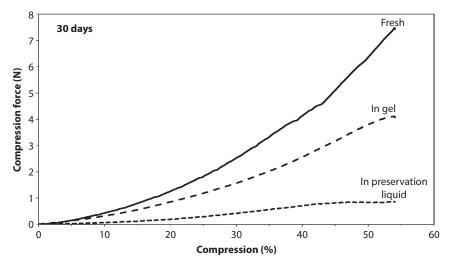
**Figure 2.21** Isoelectric focusing-PAGE analysis of the whole protein fraction from water buffalo mozzarella cheese samples stored at 8°C in its own liquid (lane b) or in gel (lane c) for 15 cl, and in its own liquid (lane d) or in gel (lane e) for 44 d. The electrophoretic profile of a freshly produced cheese sample, kept a t -20°C until the analysis, is shown in lane a.

For comparisons, disc-PAGE analysis of proteins from a freshly produced cheese sample (lane a) and from a water buffalo whole casein sample (lane b) is also included. The gel was overloaded in order to put in evidence even poor differences in the profiles. Nevertheless, the type and the extent of protein proteolysis, even after a 44-d storage period at 8°C, were quite similar to that already found in a freshly prepared sample, regardless of the environmental storage conditions (agar or liquid).

Physical properties are extremely important in order to evaluate the state of preservation of mozzarella. As matter of fact, the deformability, the resistance to break and the compactness of a food as it is witnessed during mastication, and the energy related to these operations, induce in the consumer a pool of sensorial stimuli which contribute to determine his judgment on the quality of the food. We have hence carried out mechanical tests in order to quantify the mechanical consistency of mozzarella pasta as function of time and type of storage. Samples of mozzarella (stored in liquid and in gel) were compressed in monoaxial load, by an Instron type dynamometer, recording the penetration force against the displacement. We carried out the above tests up to 30 days of storage. We reported the results after 5 and 30 days. After 5 days (Figure 2.22), which is considered the storage time at which the mozzarella is still fresh, the control sample had already witnessed a strong diminution of the compression strength, while the sample in gel still maintained very high strength. The most impressive result is recorded after 30 days of storage (Figure 2.23). In this case, the control reached a very low level of compressive strength, while the



**Figure 2.22** Compression tests of water buffalo mozzarella cheese stored for 5 d at 4°C in gel and in its own preservation liquid compared with fresh water buffalo mozzarella cheese.



**Figure 2.23** Compression tests of mozzarella cheese stored far 30 d at 4°C in gel and in its own preservation liquid compared with fresh water buffalo mozzarella cheese.

gel-stored cheese still maintained, practically unchanged, its mechanical strength.

In conclusion, the research of innovative packaging is a fundamental step towards the strategy to save the characteristics of a typical product such as water buffalo mozzarella cheese, also with a view toward reaching markets nowadays forbidden by distance and shipping costs. The innovative gels based on natural polysaccharides have the peculiar characteristic to allow the prolonged maintenance of sensorial properties of the cheese with no addition of chemical substances and with no thermal treatment on the milk.

### 2.7 Future Trends in Food Packaging

Traditional plastics are those which are most present in the food packaging sector, so they affect the weight of the waste. Moreover, the enormous variety of plastics generated contribute to the difficult process of disposal and recycling, besides generally being pollutants from exhaustible resources.

In contrast, biopolymers from renewable resources and compostables facilitate recycling, generate reusable waste as production inputs, and also ensure compliance with the requirements for food contact.

Sustainability in packaging remains a major trend with pressure from both consumers and regulators, although now accompanied by the recognition that brands should pursue a focus on achieving packaging efficiency a more holistic approach that incorporates sourcing as well as product protection, transport, display and end of life. There is of course very little value to the customer in environmentally friendly packaging if the final product arrives damaged or otherwise unfit for use.

There is, however, always a scope to improve the environmental performance of products and package design, as seen in the recognition of paper and board as a material that is renewably sourced, is easily recycled and can biodegrade at end of life.

Apparently biopolymers could be a satisfactory alternative to the exploitation of fossil resources, but do not make the mistake of adopting simple solutions. However, in the short term, it is necessary to consider what the effect would be of mass producing them.

Given the negative externalities of a hypothetical intensive agriculture associated with the generation of such biopolymers and the defined parameters of sustainable agriculture, we see how the latter makes possible the production of biomass, the main raw material of biopolymers, providing economic, environmental, social and qualitative-sensory characteristics. However, its limitations, for instance, do not make possible large-scale production for economies of scale.

Looking towards the second half of 2013 and beyond, it is clear that all of these trends are here to stay. To meet these trends and to continue delivering value to customers, the packaging industry needs continued innovation in smarter food packaging design that fuses functionality with moves to limit the impact packaging has on the environment. Packaging is a vital component in the modern food industry and pressure from all stakeholders should be welcomed as it drives innovation and better packaging design.

# References

- 1. Parisi, S., The prediction of minimum durability in dairy products through analysis of bacterial and chemical physical contents. *Italian Food Technology* 29:5–14, 2002.
- 2. UNI 10534:1995 Condizionamento alimentare. Linee guida per il condizionamento in atmosfera modificata.
- 3. Mifflin, H., ed., *The American Heritage Dictionary of the English Language*, 4th ed., Houghton Mifflin Company: Florida, 2006.
- 4. IFST, Shelf Life of Foods: Guidelines for its Determination and Prediction. Institute of Food Science and Technology, London, 1993.
- Burr, H. K., Elliott, R. P. Quality and safety in frozen foods. JAMA 174:1178– 1180, Oct 29 1960.
- Michener, H. D., Elliott, R. P. Minimum growth temperatures for food poisoning, fecal-indicator, and psychrophilic microorganisms. *Adv Food Res* 13:349–396, 1964.
- 7. Elliott, R. P., Michener, H. D. Factors affecting the growth of psychrophilic micro-organisms in foods: A review. U. S. Dept Agr Tech Bull, No. 1320, 1965.
- 8. Ayers, J. C., Ogilvy W. S., Stewart, G. F. Postmortem changes in stored meat. I: Microorganisms associated with development of slime on eviscerated cut-up poultry. *Food Technol* 4:99–205, 1950.
- 9. Barnes, R. E., Shrimpton, D. H. Causes of greening of uneviscerated poultry carcasses during storage. *J Appl Bact* 20:273, 1957.
- 10. Fruit and vegetable processing. *FAO Agricultural Services Bulletin No.119*. Food and Agriculture Organization of the United Nations Rome, 1995.
- Buchanan, R. L. Predictive food microbiology. *Trends Food Sci Technol* 4:611, 1993.
- 12. Skinner, G. E., Larkin, J. W. Mathematical modeling of microbial growth: A review. *J Food Safety* 14:175–217, 1994.
- McMeekin, T., Brown, J., Krist, K. Quantitative microbiology: A basis for food safety. *Emerging Infectious Diseases* 3 (4):541–9, 1997.

- 62 FUNCTIONAL POLYMERS IN FOOD SCIENCE
- 14. Hintlian, C. B., Hotchkiss, J. H., The safety of modified atmosphere packaging: A review. *Journal Food Technology* 40:70–76, 1986.
- Yam, K. L., Takhistov, P. T., Miltz, J., Intelligent packaging: Concepts and applications. J Food Sci 70:R1–R10, 2005.
- 16. Gander, P. The smart money is on intelligent design. *Food Manufacture* Feb: xvxvi, 2007.
- 17. Robertson, G. L. Active and intelligent packaging. In *Food Packaging: Principles and Practice*, 2nd ed. Chap. 14, CRC Press, Boca Raton, Fl., 2006.
- 18. Patrick, M. Leatherhead Food RA, personal communication, 2000.
- 19. Crompton, T. R. *Additive Migration from Plastics into Foods*, Smithers Rapra Technology Limited, Shawbury UK, 2007.
- 20. Garland, A., *Nanotechnology in Plastics Packaging*, Pira International Limited, Leatherhead, UK, 2004.
- 21. Dutta, P., Gupta, S., *Understanding of Nano Science and Technology*, Global Vision Publishing House, New Delhi, India, 2006.
- De Jong, A. R., Boumans, H., Slaghek, T., Van Veen, J., Rijk, R., Van Zandvoort, M., Active and intelligent packaging for food: Is it the future? *Food Add Contam* 22:975–979, 2005.
- Cannillo, V., Bondioli, F., Lusvarghi, L., Montorsi, M., Avella, M., Errico, M. E., Malinconico, M. Modeling of ceramic particles filled polymer-matrix nanocomposites. *Comp Sci Technol* 66:1030–1037, 2006.
- Chandra, R., Rustgi, R. Biodegradable polymers. Prog Polym Sci 23 (7): 1273– 335, 1998.
- Mohanty, A. K., Misra, M., Hinrichsen, G. Biofibers, biodegradable polymers and biocomposites: An overview. *Macromol Mater Eng* 276/277:1–24, 2000.
- 26. Platt, D. Biodegradable Polymers Market Report. Smithers Rapra Ltd, 2006.
- Kale, G., Kijchavengkul, T., Auras, R., Rubino, M., Selke, S. E., Singh, S. P. *Macromol Biosci* 7 (3): 255–277, 2007.
- Avella, M., Martuscelli, E., Raimo, M. Properties of blends and composites based on poly (3-hydroxy)butyrate (PHB) and poly (3-hydroxybutyratehydroxyvalerate) (PHBV) copolymers. *J Mater Sci* 35 (3): 523–545, 2000.
- Bonartsev, A. P., Myshkina, V. L., Nikolaeva, D. A., Furina, E. K., Makhina, T. A., Livshits, V. A., Boskhomdzhiev, A. P., Ivanov, E. A., Iordanskii, A. L., Bonartseva, G. A. Biosynthesis, biodegradation, and application of poly (3-hydroxybutyrate) and its copolymers: Natural polyesters produced by diazotrophic bacteria. In *Communicating Current Research and Educational Topics and Trends in Applied Microbiology*, Vol. 1, ed. A. Méndez-Vilas, pp. 295–307, 2007.
- Mitrus, M., Wojtowicz, A., Moscicki, L. Biodegradable polymers and their practical utility. In *Thermoplastic Starch: A Green Material for Various Industries*, eds. L. Janssen, L. Moscicki, Wiley-VCH, 2010.
- Tokiwa, Y., Calabia, B. P., Ugwu, C. U., Aiba, S. Biodegradability of plastics. *Int J Mol Sci* 10:3722–3742, 2009.

- 32. Drumright, R. E., Gruber, P. R., Henton, D. E. Polylactic acid technology. *Adv Mater* 12 (32): 1841–1846, 2000.
- 33. Auras, R., Harte, B., Selke, S. An overview of polylactides as packaging materials. *Macromol. Biosci* 4 (9): 835–864, 2004.
- Kale, G., Auras, R., Singh, S. P. Comparison of the degradability of poly (lactide) packages in composting and ambient exposure conditions. *Packag Technol Sci* 20 (1): 49–70, 2007.
- Huang, S. J., Koenig, M. F., Huang, M. Design, synthesis and properties of biodegradable composites. In *Biodegradable Polymers and Packaging*, eds. C. Ching, D. Kaplan, E. Thomas, pp. 97–112, Technomic Publishing Company, 2003.
- Tokiwa, Y., Iwamoto, A., Koyama, M. Development of biodegradable plastics containing polycaprolactone and/or starch. *Polym Preprints* 63:742–746, 1990.
- 37. Averous, L., Moro, L., Dole, P., Fringant, C. Properties of thermoplastic blends: Starch– polycaprolactone. *Polymer* 41 (11): 4157–4167, 2000.
- 38. Mani, R., Bhattacharya, M. Properties of injection moulded blends of starch and modified biodegradable polyesters. *Eu Polym J* 37 (3): 515–526, 2001.
- Avella, M., Errico, M. E., Laurienzo, P., Martuscelli, E., Raimo, M., Rimedio, R. Preparation and characterization of compatibilized polycaprolactone/starch composites. *Polymer* 41:3875–3881, 2000.
- 40. Bastioli, C., Bellotti, V., Del Tredici, G., Guanella, I., Lombi, R. Complexed starch-containing compositions having high mechanical properties. US Patent #6348524, 1999.
- 41. Bastioli, C., Raffa, G., Rallis, A. Cotton budsticks of plastic material, US Patent #5902262, 1995.
- 42. Gilbert, S. G. Food/package compatibility. Food Technol 39:54-56, 1985.
- 43. Sheperd, M. T. Trace contamination of food by migration from plastics packaging: A review. *Food Chem* 8:129–145, 1982.
- 44. Crosby, N. T. Food Packaging Material: Aspects of Analysis and Migration of Contaminates. Applied Science Publisher Ltd, 1981.
- 45. Kondyli, E., Demertzis, P. G., Kontominas, M. G. Migration of dioctylphthalate and dioctyladipate plasticizers from polyvinylchloride films into olive oil. *Food Chemistry* 36:1–10, 1990.
- 46. Sharma, G. K., Madhura, C. V., Arya, S. S., Interaction of plasticfilms with foods. 2: Effect of polyethylene and polypropylenefilms on the stability of vegetable oils. *Journal of Food Science Technology* 27:328–331, 1990.
- 47. Tawfik, M. S. and Huyghebaert, A. Interaction of packaging materials and vegetable oils: Oil stability. *Food Chemistry* 64:451–459, 1999.
- 48. Tiecco, G. Igiene e tecnologia alimentare, Calderini Ed agricole: Italia, 2001.
- 49. Zambonelli, C., Papa, F., Romano, P., Suzzi, G., Grazia, L. *Microbiologia dei salumi*; Ed. Edagricole: Bologna, Italia, 1992.
- 50. Giaccone, V. Legislazione sugli Alimenti di Origine Animale, Ed. Unipress: Padova, Italia, 1996.

- 64 FUNCTIONAL POLYMERS IN FOOD SCIENCE
- 51. Del Monte, P., Magnani, U., Monari, M. *Industria dei salumi: Igiene, tecnica e legislazione*, Ed. Edagricole: Bologna, Italia, 1990.
- 52. Simonetti, P., Cantoni, C. Attività antibatterica di lattobacilli spp., *Industrie Alimentari* Vol. XXI (4): 783–786, 1982.
- 53. Gardini, F., Lanciotti, R., Westall, F. Interazione fra microrganismi e materiali di imballaggio. In *Imballaggio funzionale per una migliore qualità degli alimenti confezionati*, Progetto RAISA, 3–4/02/1994, Conference Proceedings.
- Laurienzo, P., Malinconico, M., Volpe, M. P., Luongo, D. E., Ranieri, V., Scoponi, M. Compatibilized Ny6-based blends as innovative packaging materials: Determination of some important properties relevant to food contact application. *Packag Technol Sci* 14 (3): 109–117, 2001.
- 55. Swatland, H. J., ed., *Structure and Development of Meat Animals and Poultry*, Technomic Publishing: Lancaster, PA, 1994.
- Rossi, L. Fourth interlaboratory study of methods for determining total migration of plastic materials in liquids simulating fatty foodstuffs. *J Assoc Off Anal Chem* 64 (3): 697–703, 1981.
- 57. Ahvenainen, R. Novel Food Packaging Techniques. Woodhead Publishing: Cambridge, 2003.
- Rocha, A. M. C. N., Morais, A. M. M. B. Shelf life of minimally processed apple (c.v. Jonagored) determined by colour changes. *Food Control* 14 (1): 13–20, 2003.
- 59. Brody, A. L. Chilly is hot. Food Technology 56 (4): 102-105, 2002.
- Anese, M., Manzano, M., Nicoli, M. C. Quality of minimally processed apple slices using different modified atmosphere conditions. *J Food Quality* 20:359– 370, 1997.
- Soliva-Foruny, R. C., Martin-Belloso, O. New advances in extending the shelflife of fresch-cut fruits: A review. *Trends Food Sci Technol* 14 (9): 341–353, 2003.
- 62. Alley, E. W., Nathance P. K., Donna A. M. Factors affecting quality of fresh-cut horticultural products. *Postharvest Biol Tech* 9:115–125, 1996.
- 63. Kader, A. A. L'applicazione dell'atmosfera controllata per il mantenimento della qualità della frutta fresca. *Frutticoltura* 11:44–47, 2000.
- 64. Rocculi, P., Romani, S., Della Rosa, M. Effect of MAP with argon and nitrous oxide on quality maintenance of minimally processed kiwifruit. *Postharvest Biol Tech* 35 (3): 319–328, 2005.
- 65. Lanciotti, R., Gianotti, A., Patignani, F., *et al.* Use of natural aroma compounds to improve shelf-life and safety of minimally processed fruits. *Trends Food Sci Technol* 15 (3–4): 201–208, 2004.
- 66. Karger-Kocsis, J., ed. *Polypropylene: An A–Z Reference*. Kluwer Academic Publishers: Dordrecht, 1999.
- 67. Karian, H. G., ed. *Handbook of Polypropylene and Polypropylene Composites*. Marcel Dekker: New York, 1999.
- 68. Karger-Kocsis, J., ed. *Polypropylene: Structure, Blends and Composites.* Chapman and Hall: London, 1995.

- 69. Deanin, R. D., Manion, M. A. Compatibilization of polyolefin polyblends. In *Handbook of Polyolefins*, 2nd ed., Vasile, C., ed., pp. 575–602. Marcel Dekker: New York, 2000.
- Avella, M., Laurienzo, P., Malinconico, M., Martuscelli, E., Volpe, M. G. Functionalized polyolefins: Synthesis and application in blends and composites. In *Handbook of Polyolefins*, 2nd ed., Vasile, C., ed., pp. 723–771. Marcel Dekker: New York, 2000.
- García-López, D., Merino, J. C., Pastor, J. M. Influence of the CaCO3 nanoparticles on the molecular orientation of the polypropylene matrix. *J Appl Polym Sci* 88 (4): 947–952, 2003.
- Hasegawa, N., Okamoto, H., Kato, M., Usuki, A. Preparation and mechanical properties of polypropyleneclay hybrids based on modified polypropylene and organophilic clay. *J Appl Polym Sci* 78 (11): 1918–1922, 2000.
- 73. Svoboda, P., Zeng, C., Wang, H., Lee, L. J., Tomasko, D. L. Morphology and mechanical properties of polypropylene/organoclay nanocomposites. *J Appl Polym Sci* 85 (7): 1562–1570, 2000.
- Kawasumi, M., Hasegawa, N., Kato, M., Usuki, A., Okada, A. Preparation and mechanical properties of polypropylene-clay hybrids. *Macromolecules* 30 (20): 6333–6338, 1997.
- 75. Manias, E., Touny, A., Wu, L., *et al.* Polypropylene/montmorillonite nanocomposites: Review of the synthetic routes and materials properties. *Chem Mater* 13 (10): 3516–3523, 2001.
- Gorrasi, G., Tammaro, L., Tortora, M., *et al.* Transport properties of organic vapors in nanocomposites of isotactic polypropylene. *J Polym Sci, Part B: Polym Phys* 41 (15): 1798–1805, 2003.
- 77. Ellis, T. S., D'Angelo, J. S. Thermal and mechanical properties of a polypropylene nanocomposite. *J Appli Polym Sci* 90 (6): 1639–1647, 2003.
- European Council Regulation No. 1935/2004 of the European Parliament and of the Council of 27 October 2004 on materials and articles intended to come into contact with food and repealing Directives 80/590/EEC and 89/109/EEC, Official Journal L 338, 13/11/2004, 0004–0014.
- 79. Ahvenainen, R. New approaches in improving the shelf life of minimally processed fruit and vegetables. *Trends Food Sci Technol* 7 (6): 179–187, 1996.
- Paonessa, A. Influence of the preservation liquid of Mozzarella di Bufala Campana D. O. P. on some aspects of its preservation. Bubalus Bubalis IV:30– 36, 2004.
- Kindstedt, P. S., Zielinski, A. M., Almena-Aliste Q., Ge, M. A post-manufacture method to evaluate the effect of pH on mozzarella cheese characteristics. *Aust J Dairy Technol* 56 (Suppl. 3): 202–207, 2001.
- 82. Guinee, T. P., Feeney, E. P., Auty, M. A. E., Fax, P. F. Effect of pH and calcium concentration on some textural and functional properties of mozzarella cheese. *J Dairy Sci* 85:1655–1669, 2002.

#### 66 FUNCTIONAL POLYMERS IN FOOD SCIENCE

- 83. Almena-Aliste, Q., Ge, M., Kindsteclt, P. S. Reversibility of pH-induced changes in the calcium distribution and melting characteristics of Mozzarella cheese. *Aust J Dairy Technol* 57:3–9, 2002.
- 84. Jeremiah, J. J., Sheehan, J., Timothy, T. P., Guinee, P. Effect of pH and calcium level on the biochemical, textural and functional properties of reduced-fat mozzarella cheese. *Int Dairy J* 14 (Suppl. 2): 161–172, 2003.
- 85. Sood, V. K., Gaind, D. K., Dewan, R. K. Correlation between micelle salvation and calcium content. *NZ J Dairy Sci Technol* 14:32–34, 1979.
- 86. Feeney, E. P., Guinee, T. P., Fox P. F. Effect of pH and calcium concentration on proteolysis in mozzarella cheese. *J Dairy Sci* 85:1646–1654, 2002.
- Addeo, F., Garro, G., Intorcia, N., Pellegrino, L., Resmini, P., Chianese, L. Gel electrophoresis and immunoblotting for the detection of casein proteolysis in cheese. *J Dairy Res* 62:297–309, 1995.

# Transfer Phenomena in Food/Packaging System

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#### Abstract

Food contamination results from various interactions between food and packaging material. Migration of volatiles, additives, monomers and oligomers from packaging materials into food and adsorption of volatile compounds of food by polymer are important from a safety, hygienic and economic point of view. The term migration includes two phenomenons (partition and diffusion) that can be important for determination of contaminant concentrations in the food system at any time. Estimation of partition coefficient, K, value in the food/packaging system has been a major objective of different studies. Various parameters can influence the partition coefficient such as temperature, pH, chemical structure of migrant, molecular size and structure and fat content, and degrees of crystallinity. In addition, different practical methods are applicable for identification of volatile compounds present in polymer and food.

*Keywords:* Packaging, molecular transfer, interaction, migration, partition coefficient

# 3.1 Introduction

Packaging makes food convenient and gives greater food safety assurance from microorganisms and biochemical changes so that packaged foods can enjoy a longer shelf life. Now, more than 30 different plastics are being used as packaging materials [1]. The increasing use of plastics in food packaging

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has led to the need for more information about interactions between plastic packaging materials and foods [2,3]. Despite the fact that all polymers allow mass transport of low molecular weight substances (permeation, migration and sorption), they are extensively used in packaging due to their wide range of flexibility, size and shapes, thermal sealability, and cost [4,5].

Direct contact between plastics packaging materials and food can result in migration of low molecular weight additives from packaging material into foodstuffs [6,7]. Amounts of solvents, reaction byproducts, additives, and monomers migrating from polymer into food have been discussed by a number of scientists [8–11]. In addition, loss of low molecular weight compounds from a food into polymeric packaging materials, based on a sorption mechanism, has been the subject of considerable attention and concern [12–17]. These compounds include volatile and nonvolatile substituted. The nonvolatiles, such as fats and pigments, affect the package itself, while sorption of volatiles (flavors and aromas) more directly affects food quality, such as loss of aroma intensity [18,15,19].

Several investigations have shown that flavors can be absorbed to a considerable extent by plastic packages [20,16,21–24]. Reports have been published on partition equilibrium of aromas in packaged foods. Kwapong and Hotchkiss [12], Imai *et al.* [22], Steffen and Pawliszyn [25] and Lebossé *et al.* [26] studied the partition of aromas in packaged fruit juices or aqueous simulants.

Use of printing solvents on food packages is widespread in the food industry to inform and attract consumer attention. However, migration of residual printing ink solvents from packages to the food can cause off-flavors in food and deteriorate the quality of elaborated food products [27–29]. Solvents consist of low molecular weight compounds such as hydrocarbons, alcohols, ketones and esters [30], which can migrate to the packaged food. The kinetic (diffusion) and thermodynamic equilibrium (partition) of migration processes can be defined as an exchange of mass and energy between the packaging and food and were investigated due to the concern that human health might be endangered. Several studies reported diffusion coefficients [31] or partition coefficient values of printing ink solvents between packages and various foods [32–35] and involved finding factors that affected the partitioning behavior [36–39]. Additional data are needed on the food ingredients, solvent chemical structures and properties as related to partitioning behavior.

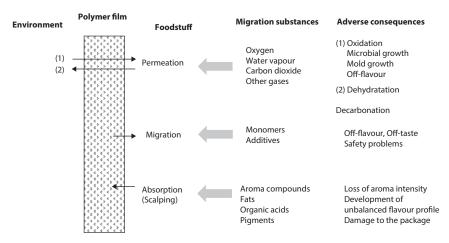
#### 3.2 Food-Packaging Interaction

Food-packaging interactions can be defined as mass or energy interplay between food, packaging, and the environment, which produces an effect on the food, and/or the package.

Mass transfer processes in packaging systems are normally referred to as permeation, migration and absorption (Figure 3.1).

Permeation is the process resulting from two basic mechanisms: diffusion of molecules across the package wall, and absorption/desorption from/into the internal/external atmospheres. Migration is the release of compounds from the plastic packaging material into the product [41]. The migration of compounds from polymer packaging materials to foods was the first type of interaction to be investigated due to the concern that human health might be endangered by the leaching of residues from the polymerization (e.g., monomers, oligomers, solvents), additives (e.g., plasticizers, colorants, UV stabilizers, antioxidants) and printing inks. Later, absorption, or scalping, of components originally contained in the product by the packaging material attracted attention. Product components may penetrate the structure of the packaging material, causing loss of aroma, or changing barrier and/or mechanical properties, resulting in a reduced perception of quality [42].

Legally, polymers for packaging are regulated through global or specific migration levels. Global migration measures the total amount of all compounds migrating into food simulants independently of migrant composition. Specific migration concerns a given migrant. Several studies have



**Figure 3.1** Possible interactions between foodstuff, polymer film and the environment, together with the adverse consequences (adapted from [40]).

measured global and specific migration from packaging materials to foods [43–46]. Authors noticed that, for specific migration measurement, and particularly with fatty foods, procedures have to be questioned because of the difficulty of analytical procedures, time consumption, or variety of simulants required [47–52].

Migration processes can be divided into three classes, based on the limiting mechanism [10,53].

- *Class 1* Non-migrating materials, with or without the presence of food. The very low diffusion into the packaging means that no measurable migration occurs.
- *Class 2* Independently migrating and not controlled by the food, although the presence of food may accelerate the migration. The high diffusion coefficient in the packaging and the low affinity between packaging and migrant mean that the migrant easily leaves the packaging material.
- *Class 3* Leaching; migration controlled by the food; negligible in the absence of food, significant in its presence. The food highly interacts with the packaging material (partial solubilization) and the low packaging/food partition coefficient make migrant transport very fast.

Even though there is no absolute cut-off between these various classes, Class 1 was applied for diffusion coefficients of less than  $10^{-15}$  m<sup>2</sup>s<sup>-1</sup>. On the other hand, Briston and Katan [54] described Class 3 systems as those that have diffusion coefficients less than  $10^{-16}$  cm<sup>2</sup>s<sup>-1</sup> in the absence of food, but  $10^{-13}$  m<sup>2</sup>s<sup>-1</sup> or higher in its presence. A migration process is fully described by the kinetics of migrant diffusion in each phase (expressed by the diffusion coefficient, D) and the chemical equilibrium (expressed by the partition coefficient, K).

# 3.3 Mass Transport Processes

The fundamental driving force in the transfer of components through a package system is the tendency to equilibrate the chemical potential. Mass transport through polymeric materials can be described as a multistep process (Figure 3.2). First, molecules collide with the polymer surface. Then they adsorb and dissolve into the polymer mass. In the polymer film, the molecules diffuse randomly as their own kinetic energy keeps them moving from vacancy to vacancy as the polymer chains move. The movement

of the molecules depends on the availability of vacancies or "holes" in the polymer film. These "holes" are formed of vacancies in the polymer film. They are formed as large chain segments of the polymer and slide over each other due to thermal agitation. The random diffusion yields a net movement from the side of the polymer film that is in contact with a high concentration or partial pressure of permeant to the side that is in contact with a low concentration of permeant. The last step involves desorption and evaporation of the molecules from the surface of the film on the downstream side [55]. Absorption involves the first two steps of this process, i.e., adsorption and diffusion, whereas permeation involves all three steps [56]. Mass transfer processes between foods and packages are governed by both kinetics and thermodynamics [9,57]. The rate at which equilibrium is attained is governed by diffusion, whereas the distribution of the migrant at equilibrium is determined by solution thermodynamics [58]. The diffusion coefficient is a kinetic parameter that provides information on migration velocity, whereas solubility and partition coefficients are thermodynamic parameters that measure migrant transfer [59,60]. Analysis of flavor scalping by packaging materials requires solubility data and calculation of partition coefficients. Strong interaction between potential migrants and polymeric matrix greatly reduces the extent of migration into contacting food [61]. Diffusion, solubility, and partition coefficients depend on the molecular dimensions of penetrants [62]. In general, as the molecular size of penetrants increases, diffusion coefficient decreases and solubility coefficient increases.

The diffusion coefficient, D(C), is a measure of the speed of molecules moving in the polymer. The solubility coefficient, *S*, is an indication of the

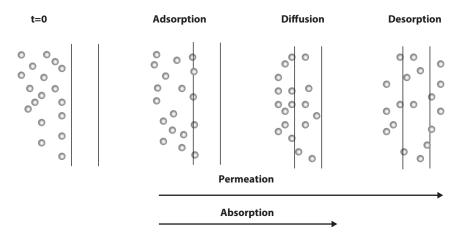


Figure 3.2 Mass transport of molecules through a plastic polymer film (data from [56]).

number of permeant molecules that are diffusing. Together, the diffusion coefficient and the solubility coefficient describe the permeability coefficient, P [56].

$$P = D(C)^*S \tag{3.1}$$

Equation 3.1 is applicable only for situations where D(C) is independent of permeant concentration *C* and *S* follows Henry's law of solubility,

$$C = Sp \tag{3.2}$$

where *p* is the partial pressure of the penetrant.

### 3.3.1 Migrant Diffusion

Quantitative measurement of the rate at which a diffusion process occurs is usually expressed in terms of diffusivity (also called the "diffusion coefficient"), expressed in  $m^2s^{-1}$ .

The classical theory used to model the diffusion process is based on Fick's laws [63,64]. Diffusion in homogeneous media is based upon the assumption that the rate of transfer, R, of a migrant passing perpendicularly through the unit area of a section is proportional to the concentration gradient between the two sides of the packaging, as:

$$R = \frac{\partial C}{\partial t} = -D(C)\frac{dC}{dX}$$
(3.3)

where D(C) is the diffusion coefficient in m<sup>2</sup>s<sup>-1</sup>. In general, *D* is a function of the local diffusant concentration, *C* (molm<sup>-3</sup>), *t*, is the time (*s*) and *X*, the thickness of the material (m). The amount of package components that may migrate from a plastic packaging material into liquid or solid food depends on the chemical and physical properties of food and polymer [65,2]. Various factors like migrant concentrations, molecular weight, solubility, diffusivity, partition coefficient between polymer and food, time, temperature, polymer and food compositions and structures (density, crystallinity, chain branching) are the main controlling factors of migration [9,66]. Legally, polymers for packaging are regulated through global or specific migration levels. Global migration measures the total amount of compounds migrated to food independently of migrants' composition. Specific migration concerns a given migrant.

Several studies measured global and specific migrations from packaging materials to foods [43–46]. Authors noticed that, for specific migration measurement, and particularly with fatty foods, procedures have to be questioned because of the difficulty of analytical procedures, time consumption, or variety of simulants required [47–49,67,45,50–52].

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### 3.3.2 Migrant Partition Coefficient

In a two-phase food/polymer system, migrant transfer from one phase to the other one occurs to reach thermodynamic equilibrium. Partition coefficient is defined as the ratio of migrant equilibrium concentration in the polymeric material,  $C_p$ , to its equilibrium concentration, in the food phase,  $C_c$ . *K* is defined as:

$$K = \frac{C_p}{C_s} \tag{3.4}$$

When K = 1, the migrant concentration in food phase equals concentration in polymeric phase, at equilibrium. *K* is higher when more migrant is absorbed into the polymer than in food. For food safety, a large *K* limits migration from packaging material to food; conversely a lower *K* indicates that more migrant is adsorbed into food. However, to minimize flavor loss in a package, a low *K* is preferred. Partition coefficient depends on the solubility coefficient, which indicates the polymer-solvent compatibility [68]. Thus, the partition coefficient may be available for predicting the cohesive property (in other words, sorption) of flavor compound for films, the cohesive energy density, *CED*, which is defined by Equation 3.5:

$$CED = \frac{\Delta E}{V} \tag{3.5}$$

where  $\Delta E$  is the energy of vaporization and *V* is the component molar volume. Due to thermodynamic relations, it is convenient to introduce a new symbol,  $\delta$  (Equation 3.6) [69,70].

$$\delta = \left(CED\right)^{1/2} \tag{3.6}$$

The dimensions of  $\delta$  are  $(calcm^{-3})^{1/2}$ , also called 1 Hildebrand (1H). The smaller the difference between the  $\delta$  values of two substances the greater the solubility parameter. Other factors important in prediction of solubility include polarity and hydrogen-bonding character of the substances. Hildebrand's solubility parameter has been investigated for use in the prediction of flavor sorption by packaging polymers [71]. Haleck and Luttmann [72] and Nielsen [73] used Hildebrand's solubility parameter to explain the sorption behavior of citrus-flavor compounds and polyolefines.

Initial efforts in prediction of flavor sorption were based on modified versions of the Hildebrand equation [74]. Hansen's equation was based on a three-dimensional map composed of dispersive, polar, and hydrogenbonding components of Hildebrand's solubility parameter ( $\delta$ ). Hansen pioneered the concept that the total cohesive energy and the total solubility parameter ( $\delta_T$ ) arises from a nonpolar (dispersive) parameter ( $\delta_D$ ), a polar parameter ( $\delta_D$ ) and a hydrogen bonding parameter ( $\delta_H$ ).

$$\delta_T = \sqrt{\delta_D^2 + \delta_P^2 + \delta_H^2} \tag{3.7}$$

Solute and solvents are represented as points in the three-dimensional Hansen solubility space. Applications in which the solubility parameter approach have been employed include finding compatible solvents for coating resins, finding an effective mass separating agent, predicting the swelling of cured elastomers by solvent, and estimating liquid-liquid equilibrium in polymer systems [70]. The Hansen equation was effectively used in the paint and pigment industry for identification of suitable solvents for paint polymers [74,75].

# 3.4 Effects of Different Parameters on Partition Coefficient

#### 3.4.1 Temperature and Duration of Contact

Storage temperature is an important parameter acting on the degree of aroma absorption by polymer [76,77].

The permeability of gases and liquids in polymers increased with increasing temperature according to the Arrhenius relationship [78,79] in the absence of glass transition. The effect of temperature on reaction rates was empirically found to produce a linear relationship between log *K* and 1/T. Arrhenius plots of ln  $K_p$  vs 1/T produced enthalpy values ( $\Delta H$ ) for the sorption from Equation 3.8:

$$\ln K_P = \frac{1}{T} \left( \frac{-\Delta H}{R_P} \right)$$
(3.8)

where *T* is absolute temperature in degrees Kelvin (*K*) and  $R_p$  is the perfect gas constant (1.98717 cal.mol<sup>-1</sup>. K<sup>-1</sup>).

In fact, the relationship is the same as that seen in the van't Hoff analyses of equilibrium constants. In an ideal equilibrium model the molecules heat of transfer between phases can be related to the equilibrium constant by the van't Hoff equation [80]. By performing a van't Hoff analysis, we can extract enthalpy and entropy changes for a reaction:

$$\ln K = \frac{-\Delta H}{R_p T} + \frac{\Delta S^{\circ}}{R_p}$$
(3.9)

The kinetics of migration are, to a first approximation, first order in that the extent of migration increases according to the square root of the time of contact.

### 3.4.2 Chemical Structure and Mobility of Migrant

The mobility of a migrant in the packaging material depends on the size and shape of the molecule, any interaction it experiences with the material, and the intrinsic resistance to mass transfer that the material presents.

The chemical structure of a migrant is an important parameter that can influence the partition coefficient. Alcohols and short-chained esters had higher partition coefficients in the oil/polymer system than in the water/ polymer one. They have a higher affinity for the plastic when they are in oil solution than when in they are water. In addition, short-chained esters are more polar, therefore are lost to a greater extent from oil than from aqueous solutions. Aldehydes have less solubility in the polymer when they are in oil, because of their long carbon nonpolar chains. As a result, they have lower partition coefficients in the oil/polymer than in the water/polymer [81]. Partition coefficients of all volatile compounds decreased with increasing ethanol concentration, although the decreasing behavior was different for each homologous series [82].

### 3.4.3 Fat Content of Foods and Degrees of Crystallinity

An and Halek [39] studied partitioning  $(K_p)$  of printing ink solvents in three different types of chocolate (cream, liquor, chips) with different fat content and different degrees of crystallinity. The KP for each solvent at 25, 35, and 45°C increased with increasing temperature. At 25°C, the partition coefficients decreased in the following order: cream (29% fat content and lowest crystallinity) > liquor (48% fat and medium crystallinity) > chips (25% fat and higher crystallinity). At this temperature, the degree of crystallinity in the structure was more important than the fat content. At 35°C, the order was: liquor (48.4% fat) > cream (28.9% fat) > chips (25.4% fat). Thus, as the structures of chocolates became less crystalline, fat content affected the partition coefficient values to a greater degree. At 45°C, the structure in each sample became more amorphous and the order of  $K_p$ value was the same as that at 35°C, but KP differences were increased.

# 3.5 Model Migrants

Model migrants of different chemical structures, polarities, hydrophobicity and molecular weight have been selected: limonene, styrene, bisphenol A, diisopropyl naphthalene (DIPN), triacetin, butylated hydroxytoluene (BHT), triclosan.... These substances cover a wide range of technical applications in plastics material, for instance (monomers, antioxidant....).

Limonene is a terpene very commonly found in recovered PET (polyethylene terephthalate). This volatile compound is a precursor to off-flavor compounds in foods and it can also be absorbed by other packaging materials such as low density polyethylene (LDPE) and polycarbonate (PC) [83].

Styrene, a monomer used in the manufacture of numerous types of plastics, can be in direct contact with food when polymers such as polystyrene and acrylenenitrile-butadiene-styrene are used as packaging materials [84].

Triacetin is an antifungal agent used in the perfume and pharmaceutical industries, although it is also used as a plasticizer in cellulose.

Diisopropylnaphthalenes (DIPN) are widely employed as solvents in the paper industry. The presence of this molecule in food products may possibly occur due to the migration from the paperboard packaging, made from recycled fibers originating from feedstock containing carbonless copy paper [85].

Bisphenol A is a monomer used to produce polycarbonate plastics [86]. It is also used as an antioxidant or inhibitor in the manufacture and processing of polyvinyl chloride (PVC) [87].

Butylated hydroxytoluene (BHT) is also commonly used as an antioxidant in plastics [88]. This molecule exhibits high mobility and therefore has a tendency to migrate rapidly from packaging materials into foods [89].

All these migrants present different chemical structures, molecular weight, and solubility polarity.

### 3.6 Instrumental Analyses

Many experimental methods have been reported to determine migrant concentrations in the polymer/food system. Gavara *et al.* [90] used three techniques, dynamic thermal stripping-thermal desorption (DTS-TD), gel permeation chromatography (GPC), and gas chromatography (GC) for partition studies of organic compounds in water/polystyrene systems. The multi-technique method is certainly a good way to validate the partition coefficients measured. The main techniques are described below.

### 3.6.1 Gas Chromatography with Flame Ionization Detector

In general, gas chromatography (GC) is the method for K determination universally applied with the help of several highly efficient modes of extraction, (pre)concentration, injection, separation, and qualitative or quantitative detection of the volatile (flavor) compounds [91]. This technique has been used to determine styrene, 1-octene, DIPN, laurolactam, ATBC and limonene.

Kwapong and Hotchkiss [12] used solvent extraction (e.g., hexane or heptane) and gas chromatography to measure sorption and partition coefficients of aroma compounds in two types of polymers (polyethylene and ionomers) in contact with aqueous solutions. Halek and Levinson [36] used GC to measure the partition coefficient of printing ink solvent polypropylene/air and cookie/air. Nielsen *et al.* [81] and Nielsen [73] used supercritical carbon dioxide extraction directly coupled with a gas chromatograph for measurements of absorbed aroma compounds in plastic packaging material and to directly collect extracted samples in the GC column for quantification. As another example, Garde *et al.* [92] used the GC method to determine the concentration of three antioxidants (AO<sub>s</sub>) from polypropylene films in fatty food simulants (heptane and 95% ethanol).

The analysis of flavor in packaging materials generally involves headspace gas chromatography techniques, which are simple and reproducible but have a low sensitivity. The headspace GC analysis was applied for identification and determination of individual components and substance present in complex mixtures.

Headspace techniques are restricted to the most volatile components [93,94,95]. The detection of flavor compounds greatly depends on their concentration and vapor pressure, as well as on the temperature and food matrix [91]. Headspace GC is used to control the content of toxic substances in biological samples, to determine volatile components in polymer materials, and for the analysis of environmental media (air and water) and food products [96].

The flame ionization detector (FID) is certainly the most popular detector used for GC analysis. Its main advantages are its low cost, universal applicability (except for carbon dioxide and formic acid), extremely wide linear range of concentration for quantitative determinations, and longterm stability (the response factors for analytes remain very constant over long periods). As a consequence of its universality, this type of detector is neither specific, nor selective.

This technique was employed by lots of authors for migrant concentration measurements. Gas chromatography with flame ionization detector and silica capillary column has been largely used for partition coefficient determination, but, it has some disadvantages such as: the selection of column depends upon the nature of the molecule to be separated, decrease accuracy of results can be obtained for the compounds for the high polar and nonpolar compound, and highly sensitive detector was necessary for measuring very low concentrations.

### 3.6.2 Gas Chromatography-Mass Spectrometry

The technique of gas chromatography–mass spectrometry (GC-MS) has had a great impact on research in the chemical and biological sciences. Mass spectrometry (MS) is an analytical spectroscopic tool primarily concerned with the separation of molecular (and atomic) species according to their mass and includes different methods for ionizing molecules (positively and negatively charged ions). The principles involved are relatively straightforward [90]. In GC-MS, electrically unchanged gaseous molecules, coming directly from the GC column, are ionized in the ion source of the instrument, either by negative-ion chemical ionization (NICI) or by electron-impact ionization (EI) [97]. The spectrum of ions so obtained (mass spectrum) is normally presented in the form of a bar diagram in which the intensities of the various ions expressed in relative percentages are plotted against the corresponding mz<sup>-1</sup> (mass to charge ratio) values [98,99]. For interpretation, GC-MS results are compared to standard picks.

This technique was used for identification of the migrant in food/packaging systems by a large number of authors including McGorrin *et al.* [29], Startin *et al.* [100], Hollifield [101], Nielsen *et al.* [102] and Lau and Wong [1]. Franz *et al.* [103] studied the functional barrier properties of multilayer recycled poly (ethylene terephtalate) bottles for soft drinks. Lebossé *et al.* [26] noticed the interactions between reactive aroma from model citrus juice with polypropylene packaging film; Nahon *et al.* [104] for the determination of flavor release from mixtures of sodium cyclamate, sucrose, and orange aroma; Sarria-Vidal *et al.* [105], Sipilãinen-Malm *et al.* [106] and Lau and Wong [1] for the determination of the migration of plasticizers from polymer materials into solid food.

Identification and quantification of the compounds need a great knowledge of the method and a good awareness of the migrant present in the packaging.

### 3.6.3 Gel Permeation Chromatography

Gel permeation chromatography (GPC) differs from the other modes of liquid chromatography. This instrument technique provides a means to separate and quantify different molecules in a solution based on molecular size. The GPC apparatus gives, by its differential refractometer, a measure directly proportional to the concentration. The equipment is so calibrated that a certain molecular weight is associated with each elution volume [107].

The GPC technique has some advantages such as the possibility to maintain all corresponding parts at high temperature (up to 140°C), the short duration of the experiment and the high flow rate applied [108]. This experimental technique was employed by Gavara *et al.* [90] to determine the partition coefficient (K) of toluene, d-limonene, and ethyl acetate between water and polystyrene. In another case, Lau and Wong [109] used GPC to describe the migration of plasticizers from food contact material into the solid foodstuff. Kubin [110] and Kedzierewicz *et al.* [111] also used a GPC for the determination of partition coefficients. A great advantage of GPC is that the column can be used for several months without effects on retention volumes or clean-up capacity [112]. A highly sensitive detector was also necessary for measuring very low concentrations. A disadvantage is the large volumes of solvent needed [113].

### 3.6.4 High Performance Liquid Chromatography

High performance (or pressure) liquid chromatography (HPLC), began as an improved analytical separation technique, and today has become a routine method in quality control and research. It is particularly useful in fields where previous analysis of large numbers of samples containing nonvolatile or thermally unstable species has required the application of tedious and often imprecise procedures. The HPLC technique is considered to be a powerful technique for component analysis in commercial preparations and food, but pure compounds from lac dye for the reference standards are not commercially available. In addition, no effective method for isolating these components from dye preparation has been reported [114-116]. During the past decade, HPLC has emerged as an excellent analytical tool for application in diverse areas. It has been further extended to examine the interaction of polymeric materials such as polyvinyl acetate (low and heavy carbon load), polymethacrylic acid (heavy carbon load), polytriphenyl methyl methracrylate (heavy carbon load) with nonvolatile food ingredients such as ascorbic acid, niacin, phenylalanine and caffeine

[117]. The basic chromatographic process consists of the partition of sample molecules between a mobile fluid and a stationary phase. The partition of sample molecules between the mobile and stationary phases may be considered as a dynamic equilibrium, both when the mobile phase is static and also during chromatographic elution. Selection of the suitable HPLC column is principally defined by the sample characteristics such as molecular weight, solubility and polarity. Small and nonionic molecules are separated by adsorption, reversed-phase, or on chemically bonded phases, respectively. Charged samples are separated by ion-exchange, ionpair, or ion chromatography. The following stationary phases should be installed in a HPLC laboratory, which is supposed to solve rather different separation problems:

Silica gel, reversed phase (C-18), strong cation-exchanger, strong anionexchanger, and water are, respectively, solvent compatible gel columns. In HPLC, the selection of a mobile phase depends on the stationary phase. The mobile and the stationary phase have to exist together and must not destroy each other. Normally, nonpolar mobile phases will be for the adsorption chromatography, and polar mobile phases for the reversed-phase and ionexchange chromatography [116]. The HPLC techniques offer the advantage of tolerating lower sample purity, smaller size, and being dynamic range. Another advantage of HPLC is that closed, reusable columns are used, thus hundreds of samples can be run through an individual column without repackaging [118]. As an example, Snyder and Breder [119] used liquid chromatography to determine migration of styrene from polystyrene into several food stimulants. In addition, Hammarling et al. [120] determined migration of bisphenol-A diglycidyl ether (BADGE) from cans into food by HPLC. Nerín et al. [121] used it for identification of bisphenol-type contaminants from food packaging materials in aqueous foods. Papilloud and Baudraz [122] applied HPLC for the determination of printing inks from packaging in food.

#### 3.6.5 Liquid-Liquid and Solid-Phase Extractions

Liquid-liquid extraction (LLE) and solid-phase extraction (SPE) are nowadays the most important procedures of organic sample preparation [123].

Liquid-liquid extraction (LLE) applies to liquid matrices. It relies on a "partition coefficient" between two immiscible solvents for the compounds that are trying to be extracted or separated. Liquid extractions employ immiscible solvents for partitioning the compounds of interest from one

solvent to another. The LLE extractors are large sized, use considerable amounts of solvent and must be controlled in terms of stirring [123,124].

Around 1980, a smaller open-bed column, solid-phase extraction (SPE), cleanup column was introduced which could accommodate a smaller sample size. The SPE method was developed as an alternative to LLE for the separation, purification, concentration and/or solvent exchange of solutes for solutions. Solid phase extraction reduces the quantity of solvent used per analysis. It is one of the simplest, most effective and most versatile methods of sample preparation. It is supposed that the sorption behavior in SPE depends principally on the hydrophobic interaction between the sorbent and the analyte. Therefore, information about the hydrophobic characteristics of sorbents and analytes is important for the effective use of SPE [125]. The SPE method is widely used for liquid sample preparation and is based on using cartridges packed with octadecyl-silica gel or other sorbents based on a reversed-phase mechanism. The SPE columns are packed with a selectivity packing material, such as silica gel, C-18, or ion exchange material, and the sample extract is fractionated by polarity, water solubility or ionic attraction [126,127].

The advantages of SPE and LLE are that they need less solvent, their cost is reasonable and they are rapid; in addition they have better precision and accuracy. Chuang *et al.* [128] evaluated SPE for determining pesticides in baby foods and adult duplicate-diet samples. López *et al.* [129] used this method for the quantitative determination of important wine odorants.

### 3.6.6 Solid-Phase Microextraction

In the early 1990s, solid-phase microextraction (SPME) was developed by Arthur and Pawliszyn [130]. It is a single-step, solvent-free extraction technique for volatile compounds extraction, with a high sensitivity, sample preparation technique, a reasonable cost and a rapid analysis [130,131]. It can be applied to the analysis of volatile and nonvolatile compounds in solid, liquid, and gaseous samples, especially for quickly screening the volatile composition [132]. The application of this technique was used to analyze coffee, a butter flavor in vegetable oil [132], flavor compounds in a fruit beverage [133] and orange juice [25], volatile compounds in tomato and strawberry fruit [134], and volatile compounds in vodkas [135].

The key component of the SPME device is a piece of fused silica fiber (ca.1 cm in length) coated with an adsorbent such as poly(dimethylsilomane) [132]. The principle of SPME technology is the partitioning process of the analyte between the fiber coating and the sample. At equilibrium, the

relationship can be expressed as the partition coefficient (K) between the fiber and sample [136]. The SPME technique consists of a two-step process, including the absorption of analytes onto the fiber and the desorption of analytes into an analytical instrument [137]. Good linearity of response was exhibited by SPME for volatiles ranging in concentration from ppb to ppm with negligible effects from matrix variations. The sampling of SPME should be sensitive enough to be used for dynamic investigations of impact volatiles [138]. However, SPME analysis is quite sensitive to experimental conditions such as heating temperature and time, sample volume, concentration, sample pH, sample matrix and uniformity [132,139]. Several disadvantages related to fiber stability and sensitivity have been pointed out. The main disadvantage of SPME in the field is its lack of robustness. The needle can be easily bent, and the fiber can be broken when handled without sufficient care.

### 3.6.7 Sensory Evaluation

Sensory evaluation is used to evaluate the transfer of migrants from the packaging material to food and the effect of those migrants on the development of off-flavor in the food. Threshold values are important parameters for (off-)flavor perception, which is determined by the nature and quantity of the flavor compound and the availability of such compound to the sensory system as a function of time. Moreover, food matrix plays an important role in flavor perception [140]. Taste recognition threshold concentrations (TRTC) of plastic material or printing ink solvents are determined by using different panels and rating scale evaluations of intensity, or by forced choice methods such as the triangle test [141]. The extent of residual solvent migration from packaging materials into the food can be evaluated after exposing water, food simulant, or actual food to packaging materials at 40°C, at ambient temperature, or at actual cooking temperature [141-143]. Sensory evaluation can be paralleled with objective instrumental analyses and high correlations between sensory and instrumental results can be obtained [144,145].

# 3.7 Conclusion

The protection of food is a key function of a package, and the visual and aesthetic image created by the packaging is now a sales strategy of the same order as the quality of the food product itself. As a result, the packaging technologist has to be able to tailor his product in order to reduce the level of food contamination from packaging materials. Packaging scientists and food manufacturers have worked together for marketing products that are more and more attractive and safe to the public.

In conclusion, the migration process can be important in terms of additives in the polymeric packaging material of food or the volatile compounds of food to packaging. Several factors such as the chemical and physical structure of food, packaging and migrant, concentration and mixture of migrant, fat and water contents of the food, affect the partitioning of migrants between food and packaging. Storage temperature is the most important environmental variable affecting the distribution process. In high temperature, absorption of flavor increases in the packaging material.

The other factors that affect absorption include molecular size of aroma compounds and polarity and solubility properties of both the polymers and the aroma compounds.

In the methodology, each method has some advantage and disadvantage. Both GC and HPLC were based on molecular size and polarity. They have been developed for detecting pesticides in food or transfer of migrant (volatile compound) in packaging. The GC-MS technique has the advantage of increasing the sensitivity of the analysis. The most universally applicable clean-up method is GPC for direct measurement of the migrant concentration, with minimum sample manipulation. SPE, SPME and LLE are good methods for extraction that can be used for determining the minimum sample concentration.

The SPME method can be used as a substitution and improvement of classical sample preparation methods. Thus, it can be applied for the analysis of drugs, methabolites, environmental pollution and food toxicity. Although SPE methods are becoming increasingly popular, nearly all analytical problems can be solved by LLE and SPE. Therefore, these methods can be characterized as universal from a scientific and technical view.

# References

- 1. Lau, O. W., and Wong, S. K. Contamination in food from packaging material. *Journal of Chromatography: A* 882:255–270, 2000.
- Halek, G. W. Relationship between polymer structure and performance in food packaging applications. In *Food and Packaging Interactions*, ed. J. H. Hotchkiss, pp. 195–202, Washington, DC: American Chemical Society, 1988.

- 3. Franz, R., and Brandsch, R. Migration of acrylic monomers from methacrylate polymers: Establishing parameters for migration modelling. *Packaging Technology and Science* 26:435–451, 2013.
- 4. Hernandez-Muñoz, D. H., Catala, R., and Gavara, R. Food aroma partition between packaging materials and fatty food simulants. *Food Additives and Contaminants* 18:673–682, 2001.
- Mattioli, S., Peltzer, M., Fortunati, E., Armentano, I., Jiménez, A., and Kenny, J. M. Structure, gas-barrier properties and overall migration of poly (lactic acid) films coated with hydrogenated amorphous carbon layers. *Carbon* 63:274–282, 2013.
- 6. Figge, K. *Plastic Packages for Foodstuffs*, p. 77, Stuttgart: Wissenschaftliche Verlasgesellschaft mbH, 1996.
- Huang, C., Zhu, J., Chen, L., Li, L., and Li, X. Structural changes and plasticizer migration of starch-based food packaging material contacting with milk during microwave heating. *Food Control* 36:55–62, 2014.
- 8. Koros, W. J., and Hopfenberg, H. B. Scientific aspects of migration of indirect additives from plastics to food. *Food Technologist* 33:56–60. 1979.
- 9. Gilbert, S. G., Miltz, J., and Giacin, J. R. Transport considerations of potential migrants from food packaging materials. *Journal of Food Processing and Preservation* 4:27–49, 1980.
- Downes, T. W. Practical and theoretical considerations in migration. In *Food Product-Package Compatibility*, ed. J. E. Gray, B. Harte, and J. Miltz, pp. 44– 58. PA: Technomics Publishing, 1987.
- 11. Risch, S. J. Scientific status summary: Migration of toxicants, flavours and odour- active substances from flexible packaging materials to food. *Food Technologist* 7:95–102, 1988.
- 12. Kwapong, O. Y., and Hotchkiss, J. H., Comparative sorption of aroma compounds by polyethylene and ionomer food-contact plastics. *Journal of Food Science* 52:761–763, 785, 1987.
- 13. Mannheim, C. H., Miltz, J., and Letzter, A. Interaction between polyethylene laminated carbons and aseptically packed citrus juices. *Journal of Food Science* 52:737–740, 1987.
- 14. Shimoda, M., Ikegami, T., and Osajima, Y. Sorption of flavour compounds in aqueous solution into polyethylene film. *Journal of the Science of Food and Agriculture* 42:157–163, 1988a.
- Hirose, K., Harte, B. R., Giacin, J. R., Miltz, J., and Stine, C. Sorption of d-limonene by sealant films and effect on mechanical properties. In *Food* and *Packaging Interactions*, ed. J. H. Hotchkis, pp. 28–41. Washington, DC: American Chemical Society, 1988.
- Halek, G. W., and Meyers, M. A. Comparative sorption of citrus flavour compounds by low-density polyethylene. *Packaging Technology & Science* 2:141-146, 1989.
- 17. Giacin, J. R. Factors affecting permeation, sorption, and migration processes in package-product systems. In *Foods and Packaging Materials-Chemical*

#### 86 FUNCTIONAL POLYMERS IN FOOD SCIENCE

*Interactions*, ed. P. Ackermann, M. Jãgerstad, and T. Ohlsson, pp. 12–22. Cambridge, Great Britain: The Royal Society of Chemistry, 1995.

- 18. Landois-Garza, J., and Hotchkiss, J. H., Plastic packaging can cause aroma sorption. *Food Engineering (April)*: 39–42, 1987.
- 19. Sadler, G. D., and Braddock, R. J. Oxygen permeability of low-density polyethylene as a function of limonene absorption: An approach to modelling flavour scalping. *Journal of Food Science* 55:587–588, 1990.
- Mannheim, C. H., Miltz, J., and Passy, N. Interactions between aseptically filled citrus products and laminated structures. In *Food and Packaging Interactions*, pp. 68–82. Washington, DC: American Chemical Society, 1988.
- Hansen, A. P., and Arora, D. K. Loss of flavour compounds from aseptically processed food products packaged in aseptic containers. In *Barrier Polymers and Structures*, pp. 318–332. Washington, DC: American Chemical Society, 1990.
- 22. Imai, T., Harte, B. R., and Giacin, J. R. Partition distribution of aroma volatiles from orange juice into selected polymeric sealant films. *Journal of Food Science* 55:158–161, 1990.
- 23. Ikegami, T., Nagashima, K., Shimoda, M., Tanaka, Y., and Osajima, Y. Sorption of volatile compounds in aqueous solution by ethylene-vinyl alcohol copolymer films. *Journal of Food Science* 56:500–509, 1991.
- 24. Sadler, G. D., and Braddock, R. J. Absorption of citrus flavour volatiles by low density polyethylene. *Journal of Food Science* 56:35–37, 54, 1991.
- 25. Steffen, A., and Pawliszy, J. Analysis of flavour volatiles using headspace solid-phase microextraction. *Journal of Agricultural and Food Chemistry* 44:2187–2193, 1996.
- 26. Lebossé, R., Ducruet, V., and Feigenbaum, A. Interactions between reactive aroma compounds from model citrus juice with polypropylene packaging film. *Journal of Agricultural and Food Chemistry* 45:2836–2842, 1997.
- 27. Gilbert, S. G. Migration of minor constituents from food packaging materials. *Journal of Food Science* 41:955–958, 1976.
- 28. Piringer, O. Interactions between packaging and food consequences for manufactures and consumers. Paper presented at a Meeting on Food Packaging at SIK-The Swedish Food Institute, May 29, 1986.
- 29. McGorrin, R. J., Pofahl, T. R., and Croasmun, W. R. Identification of musty component from an off-flavour packaging film. *Analytical Chemistry* 59:1109A-1112A, 1987.
- Kumai, M., Koizumi, A., Saito, K., Sakurai, H., Inoue, T., Takeuchi, Y., Ogata, M., Matsushita, T., and Ikeda, M. A nation-wide survey on organic solvent compounds in various solvent products: II. Heterogeneous products such as paints, inks and adhesives. *Industrial Health* 21:185–197, 1983.
- Desobry, S., Michalski, M. C., Mousavi, M., and Hardy, J. Static head space GC for contaminant diffusivity measurement through LDPE film. *Packaging Technology and Science* 10:229–236, 1997.

- Heydanek, M. G. Jr., Woolford, G., and Baugh, L. C. Premiums and coupons as a potential source of objectionable flavour in cereal product. *Journal of Food Science* 44:850–854, 1979.
- 33. Halek, G. W., and Hatzidimitriu, E. Partition coefficients of food package printing ink solvents in soybean oil, chocolate liquor, and a high fat baked product. *Journal of Food Science* 53:568–570, 596, 1988.
- Arab-Tehrany, E., Fournier, F., and Desobry, S. Simple method to calculate partition coefficient of migrant in food simulant/polymer system. *Journal of Food Engineering* 77:135–139, 2006.
- Arab-Tehrany, E., Mouawad, C., Desobry, S. Determination of partition coefficient of migrants in food simulants by the PRV method. *Food Chemistry* 105:1571–1577, 2007.
- Halek, G. W., and Levinson, J. J. Partitioning behaviour and off-flavour thresholds in cookies from plastics packaging film printing ink compounds. *Journal of Food Science* 53:1806–1808, 1822, 1988.
- 37. Halek, G. W., and Levinson, J. J. Partitioning and absolute flavour threshold interactions of aliphatic and aromatic food packaging solvents in high-fat cookies. *Journal of Food Science* 54:173–176, 1989.
- Halek, G. W., and Chan, A. Partitioning and absolute flavour threshold interactions of aliphatic food packaging solvent homologs in high-fat cookies. *Journal of Food Science* 59:420–423, 1994.
- An, D. J., and Halek, G. W. Partitioning of printing ink solvents on chocolate. *Journal of Food Science* 60:125–127, 1995.
- 40. Nielsen, T. J., and Jãgerstad, M. Flavour scalping by food packaging. *Trends in Food Science and Technology* 5:353–356, 1994.
- 41. Hernandez, R. J., and Gavara, R. *Plastics Packaging-Methods for Studying Mass Trasfer Interactions*, pp. 53. UK: International, Leatherhead, 1999.
- 42. Johansson, F. *Polymer Packages for Food-Materials, Concepts and Interactions: A Literature Review*, pp. 118. Göteborg: SIK- The Swedish Institute for Food and Biotechnology, 1993.
- 43. Goydan, R., Schwope, A. D., Reid, R. C., and Cramer, G. High-temperature migration of antioxidants from polyolefines. *Food Additives and Contaminants* 7:323–337, 1990.
- Lickly, T. D., Bell, C. D., and Lehr, K. M. The migration of Irganox 1010 antioxidant from high-density polyethylene and polypropylene into a series of potential fatty-food simulants. *Food Additives and Contaminants* 7:805–814, 1990.
- 45. Baner, A., Bieber, W., Figge, K., Franz, R., and Piringer, O. Alternative fatty food simulants for migration testing of polymeric food contact materials. *Food Additives and Contaminants*, 9:137–148, 1992.
- Boone, J., Lox, F., and Pottie, S. Deficiencies of polypropylene in its use as a food packaging material: A review. *Packaging Technology & Science* 6:277– 281, 1993.

#### 88 FUNCTIONAL POLYMERS IN FOOD SCIENCE

- 47. Rossi, L. Interlaboratory study of methods for determining global migration of plastics materials in liquids simulating fatty foodstuffs. *Journal of the Association of Official Analytical Chemists* 60:1282–1290, 1977.
- 48. Rossi, L. Fourth interlaboratory study of methods for determining total migration of plastics materials in liquids simulating fatty foodstuffs. *Journal of the Association of Official Analytical Chemists* 64:697–703, 1981.
- Gramiccioni, L., Di Prospero, P., Milana, M. R., Di Marzio, S., and Marcello, I. Global migration from plastic materials into olive oil and iso-octane: An experimental comparison. *Food and Chemical Toxicology* 24:23–26, 1986.
- Baner, A. L., Franz, R., and Piringer, O. Alternative methods for the determination and evaluation of migration potential from polymeric food contact materials. *Deutsch Lebensmittel Rundschau* 90:137–143, 1994.
- Bourges, F., Bureau, G., and Pascat, B. Effects of electron beam irradiation on the migration of antioxidants and their degradation products from commercial polypropylene into food simulating liquids. *Food Additives and Contaminants* 10:443–452, 1993.
- 52. Hamdani, M., and Feigenbaum, A. Migration from plasticized poly (vinyl chloride) into fatty media: Importance of simulant selectivity for the choice of volatile fatty simulants. *Food Additives and Contaminants* 13:717–729, 1996.
- 53. Kim-Kang, H. Volatiles in packaging materials. *Food Science and Nutrition* 29:255–271, 1990.
- 54. Briston, J. H., and Katan, L. L. *Plastics in Contact with Food*, pp. 466. London, England: Food Trade Press, 1974.
- 55. Singh, R. P., and Heldman, D. R. *Introduction to Food Engineering*, pp. 499. New York: Academic Press, Inc, 1993.
- Delassus, P. T. Barrier polymers. In *The Wiley Encyclopedia of Packaging Technology*, ed. A. L. Brody and K. S. Marsh, pp. 71–77. New York: John Wiley & Sons, Inc, 1997.
- 57. Strandburg, G., Howell, B. A., and Delassus, P. T. Diffusion and sorption of linear esters in a vinylidenechloride/vinylchloride copolymer film. *ACS Polymer Preprints* 30:32–33, 1989.
- Karayanni, S. T., Demertzis, P. G., and Kontominas, M. G. Adsorption of vinylchloride onto plasticized polyvinylchloride by classical partition in the presence of various food simulating solvents: Migration aspects. *Lebensmittel-Wissenschaft und- Technologie* 20:202–206, 1987.
- 59. Koszinwski, J., and Piringer, O. Food/package compatibility and migration. *Journal of Plastic Film Sheeting* 3:96–111, 1987.
- 60. Desobry, S. Transfert de matière dans les systèmes alimentaires multi- composants, Habilitation a diriger des recherches I. N. P. L. In *Biotechnologiques et industries alimentaires*, pp. 103. Nancy, France, 1998.
- 61. Orr, A., Gilbert, S. G., and Miltz, J. The interaction between acrylonitrile and acrylonitrile-styrene copolymer by invers gas chromatography. *Journal of Food Processing and Preservation* 5:179–189, 1981.

- 62. Koros, W. J. *Barrier Polymers and Structures*, pp. 406. Washington, DC: American Chemical Society, 1990.
- 63. Stannet, V. Simple gases. In *Diffusion in Polymers*, ed. J. Crank, and G. J. Park, pp. 45–56. New York, Academic Press, 1968.
- 64. Crank, J. *The Mathematics of Diffusion*, pp. 44–68, Oxford, UK: Clarendon Press, 1975.
- 65. Shepherd, M. J. The trace contamination of foods by migration from plastics packaging: A review. *Food Chemistry* 8:129–145, 1982.
- Chang, S., Guttman, C. M., Sanchez, I. C., and Smith, L. E. Theoretical and computational aspects of migration of package components to food. In *Food and Packaging Interactions*, ed. J. Hotchkiss, ACS Symposium Series 365, pp. 106–117, 1988.
- De Kruijf, N., and Rijk, M. A. H. Iso-octane as fatty food simulant: Possibilities and limitations. In *Food Additives and Contaminants; Fifth International Symposium on Migration* 5, Suppl. 1: pp. 467–483, 1988.
- Mangaraj, D. Cohesive-energy-density of high polymers. *Makromolekulare Chemie* 67:29–38, 1963.
- 69. Hilderbrand, J. H., and Scott, R. L. *The Solubility of Non-electrolytes*, 3rd ed., pp. 488, New York: Reinhold, 1959.
- Grulke, E. A. Solubility parameter values. In *Polymer Handbook*, ed. J. Brandrup, and E. H. Immergut, pp. 519–559. New York, NY: John Wiley & Sons, Inc, 1989.
- Paik, J. S. Predictive models for estimation of flavour sorption by packaging polymers. In *Foods and Packaging Materials-Chemical Interactions*, ed. P. Ackermann, M. Jägerstad, and T. Ohlsson, pp. 51–58. Cambridge: The Royal Society of Chemistry, 1995.
- Halek, G. W., and Luttmann, J. P. Sorption behaviour of citrus-flavour compounds in polyethylenes and polypropylenes: Effects of permeant functional groups and polymer structure. In *Food and Packaging Interaction*, 2nd ed. J. H. Hotchkiss, ACS Symposium Series 473, pp. 212–226. Washington, DC: American Chemical Society, 1991.
- Nielsen, T. J. Limonene and micrene sorption into refillable polyethylene teriphthalate bottles, and washing effects on removal of sorbed compounds. *Journal of Food Science* 53:253–257, 1994.
- 74. Hansen, C. M. The three dimentional solubility parameter-key to paint component affinities. *Journal of Paint Technology* 39:104–117, 1967.
- 75. Burrell, H. Solubility parameters for film formers. *Official Digest-Federation* of Paint and Varnish Production Clubs 27:726–731, 1955.
- Hall, G., and Andersson, J. Volatile fat oxidation products II: Influence of temperature on volatility of saturated, mono- and di-unsaturated aldehydes in liquid media. *Lebensmittel-Wissenschaft + Technologie* 16:362–366, 1983.
- 77. Overbosch, P., Afterof, W. G. M., and Haring, P. G. M. Flavour release in the mouth. *Food Reviews International* 7:137–184, 1991.

- 90 FUNCTIONAL POLYMERS IN FOOD SCIENCE
  - 78. Espenson, J. H. *Chemical Kinetics and Reaction Mechanisms*, pp. 142. New York: McGraw-Hill, 1981.
  - 79. Katakis, D., and Gordon, G. *Mechanisms of Inorganic Reactions*, pp. 384. New York: Wiley-Interscience, 1987.
  - 80. Moore, R. E. *Interval Analysis*, pp. 145. New Jersey, USA: Englewood Cliffs, Prentice-Hall, 1966.
  - Nielsen, T. J., Jãgerstad, M. I., and Õste, R. E. Study of factors affecting the absorption of aroma compounds into low-density polyethylene. *Journal of the Science of Food and Agriculture* 60:377–381, 1992.
  - Hwang, Y. H., Matsui, T., Hanada, T., Shimoda, M., Matsumoto, K., and Osajima, Y. Desorption behaviour of sorbed flavour compounds from packaging films with ethanol solution. *Journal of Agricultural and Food Chemistry* 48:4310–4313, 2000.
  - 83. Van Willige, R. W. G., Linssen, J. P. H., Legger-Huysman, A., and Voragen, A. G. J. Influence of flavour absorption by food packaging materials (lowdensity polyethylene, polycarbonates and polyethylene terephthalate) on taste perception of a model solution and orange juice. *Food Additives and Contaminants* 20:84–91, 2003.
  - 84. Silva, C. F., De Carvalho, R. C., and Cardeal, Z. Solidphase microextraction method the quantitative analysis of styrene in water. *Journal of Chromatographic Science* 38:315–318, 2000.
  - 85. Boccacci, M. M., Chiaccherini, E., and Gesumundo, C. Potential migration of diisopropyl naphthalenes from recycled paperboard packaging into dry foods. *Food Additives and Contaminants* 16:207–213, 1999.
  - Mountfort, K. A., Kelly, J., Jickells, S. M., and Castle, L. Investigations into the potential degradation of polycarbonate baby bottles during sterilization with consequent release of bisphenol A. *Food Additives and Contaminants* 14:737–740, 1997.
  - 87. Lopez Cervantes, J., and Paseiro Losada, P. Determination of bisphenol A in, and its migration from, PVC stretch film used for food packaging. *Food Additives and Contaminants* 20:596–606, 2003.
  - Tombesi, N. B., and Freije, H. Application of solid-phase microextraction combined with gas chromatography-mass spectrometry to the determination of butylated hydroxytoluene in bottled drinking water. *Journal of Chromatography A* 963:179–183, 2002.
  - 89. Wessling, C., Nielsen, T., Leufven, A., and Jägerstad, M. Mobility of alfatocopherol and BHT in LDPE in contact with fatty food simulants. *Food Additives and Contaminants* 15:709–715, 1998.
  - Gavara, R., Hernandez, R. J., and Giacin, J. Methods to determine partition coefficient of organic compounds in water/polystyrene systems. *Journal of Food Science* 61:947–952, 1996.
  - 91. Mariaca, R., and Bosset, J. O. Instrumental analysis of volatile (flavour) compounds in milk and dairy products. *Lait* 77:13–40, 1997.

- Garde, J. A., Catala, R., Gavara, R., and Hernandez, J. R. Characterizing the migration of antioxidants into fatty food simulants. *Food Additives and Contaminants* 18:750–762, 2001.
- 93. McNeal, T. P., and Hollifield, H. C. Quantitative multiresidue analyses for volatile organics in water and milk, using a fused silica open-tubular widebore capillary column and automated headspace gas chromatography. *Journal of the Association of Official Analytical Chemists* 73:328–331, 1990.
- 94. Ulberth, F. Headspace gas chromatographic estimation of some yoghurt volatiles. *Journal of the Association of Official Analytical Chemists* 74:630–634, 1991.
- Gaãfar, A. M. Volatile flavour compounds of yoghurt. International Journal of Food Science & Technology 27:87–91, 1992.
- 96. Ioffe, B. V., and Vitenberg, A. G. *Head-Space Analysis and Related Methods in Gas Chromatography*, pp. 276. New York: John Wiley & Sons, 1984.
- 97. Tsikas, D. Affinity chromatography as a method for sample preparation in gas chromatography/mass spectrometry. *Journal of Biochemical and Biophysical Methods* 49:705–731, 2001.
- 98. Roboz, J. Introduction to Mass Spectrometry Instrumentation and Technique, pp. 539. New York: Wiley-Interscience, 1968.
- 99. Faull, K. F., and Barchas, J. D. Negative-ion mass spectrometry fused-silica capillary gas chromatography of neurotransmitters and related compounds. In *Methods of Biochemical Analysis*, ed. DD. Glick, pp. 325–383. New York; Chichester; Brisbane: An Interscience, John Wiley & Sons, 1983.
- 100. Startin, J. R., Sharman, M., Rose, M. D., Parker, I., Mercer, A. J., Castle, L., and Gilbert, J. Migration from plasticized films into foods: 1. Migration of di-(2-ethylhexyl) adipate from PVC films during home-use and microwave cookie. *Food Additives and Contaminants* 4:385–398, 1987.
- 101. Hollifield, H. C. Food and drug administration studies of high-temperature food packaging. In *Food and Food and Packaging Interactions II*, ed. RR. J. Risch, and J. H. Hotchkiss, ACS Symposium Series 473, pp. 22–36, Washington, DC: American Chemical Society, 1991.
- 102. Nielsen, T., Damant, A. P., and Castle, L. Validation studies of a quick test for predicting the sorption and washing properties of refillable plastic bottles. *Food Additives and Contaminants* 14:685–693, 1997.
- 103. Franz, R., Huber, M., Piringer, O. G., Damant, A. P., Jickells, S. M., and Castle, L. Study of functional barrier properties of multilayer recycled poly (ethylene terephthalate) bottles for soft drinks. *Journal of Agricultural and Food Chemistry*, 44:892–897, 1996.
- 104. Nahon, D. F., Navarro y Koren, P. A., Roozen, J. P., and Posthumus, M. A. Flavour release from mixtures of sodium cyclamate, sucrose, and an orange aroma. *Journal of Agricultural and Food Chemistry* 46:4963–4968, 1998.
- 105. Sarria-Vidal, M., de la Montana-Miguelez, J., and Simal-Gandara, J. Toward a test of overall migration from the coated face of a recycled paperboard food

contact material into fatty food. *Journal of Agricultural and Food Chemistry*, 45:2701–2707, 1997.

- 106. Sipilãien-Malm, T., Latva-Kala, K., Tikkanen, L., Suihko, M. L., and Skyttã, E. Purity of recycled fibre-based materials. *Food Additives and Contaminants*, 14:695–703, 1997.
- 107. Determann, H. *Gel Chromatography*, pp. 87–136. New York: Springer-Verlag New York Inc, 1968.
- Simpson, C. F. Separation modes in HPLC. In *HPLC in Food Analysis*, ed. R. Macrae, pp. 80–121. New York: Academic Press Inc, 1982.
- Lau, O. W., and Wong, S. K. Mathematical model for the migration of plasticisers from food contact materials into solid food. *Analytica Chimica Acta* 347:249–256, 1997.
- 110. Kubin, M. A model of the mechanism of the separation of macromolecules in gel permeation chromatography on a packing with non-homogeneous pores. *Journal of Chromatography A* 108:1–12, 1974.
- 111. Kedzierewicz, F., Thouvenot, P., Monot, I., Hoffman, M., and Maincent, P. Influence of different physicochemical conditions on the release of indium oxine from nanocapsules. *Journal of Biomedical Materials Research*, 39:588– 593, 1998.
- 112. Ahmed, F. E. Analyses of pesticides and their metabolites in foods and drinks. *TrAC Trends in Analyses Chemistry* 20:649–661, 2001.
- 113. Ahmed, N., Guo, L., Mandarakas, P., Appleby, S., and Bugueno, G. Passive diffusion through polymeric membranes: a novel cleanup procedure for analysis of azinphos-methyl and azinphos-ethyl residues in fruits and vegetables. *Journal of AOAC International* 78:1450–1454, 1995.
- Ettre, L. S. Evaluation of liquid chromatography: A historical overview. In *High-Performance Liquid Chromatography: Advances and Perspectives*, vol. 1, pp. 330, New York: Academic Press. Inc, 1980.
- 115. Macrea, R. Introduction to applications of HPLC to food analysis. In Food Science and Technology a Series of Monographs: HPLC in Food Analysis, ed. RR. Macrea, pp. 1–26. London: Macrae-Academic Press Inc, 1982.
- 116. Nissen, H. P., and Kreysel, H. W. Separation systems and instrumentation in high performance liquid chromatography. In *Food Control and Research*, ed. R. Matissek, and R. Wittkowski, Hamburg: Behr's Verlag, 1992.
- 117. Khurana, A. L., and Ho, C. T. Determination of food-packaging interactions by high-performance liquid chromatography. In *Food and Packaging Interactions II*, ed. S. J. Risch, and J. H. Hotchkiss, ACS Symposium Series 473, pp. 161–173. Washington, DC: American Chemical Society, 1991.
- Hancock, W. S. Introduction to high performance liquid chromatography. In Handbook of HPLC for the Separation of Amino Acides, Peptides, and Proteins, vol. 1, pp. 3–11. Florida: CRC Press. Inc,
- 119. Snyder, R. C., and Breder, C. V., 1985, New FDA migration cell used to study migration of styrene from polystyrene into various solvents. *Journal of the Association of Official Analytical Chemists*, 68, 770–775.

- 120. Hammarling, L., Gustavsson, H., Svensson, K., and Oskarsson, A. Migration of bisphenol-A ether (BADGE) and its reaction products in canned foods. *Food Additives and Contaminants* 17:937–943, 2000.
- 121. Nerín, C., Philo, M. R., Salafranca, J., and Castle, L. Determination of bisphenol-type contaminants from food packaging materials in aqueous foods by solid-phase microextraction-high-performance liquid chromatography. *Journal of Chromatography A* 963:375–380, 2002.
- 122. Papilloud, S., and Baudraz, D. Migration testes for substrates printed with UV ink systems in aqueous simulants. *Progress in Organic Coatings* 45:231–237, 2002.
- Peñalver, A., Pocurull, E., Borrull, F., and Marcé, R. M. Trends in solid-phase microextraction for determining organic pollutants in environmental samples. *Trends in Analytical Chemistry* 18:557–568, 1999.
- 124. Zhang, N., Hoffman, K. L., Li, W., Rossi, D. T. Semi-automated 96-well liquid-liquid extraction for quantitation of drugs in biological fluids. *Journal of Pharmaceutical and Biomedical Analysis* 22:131–138, 2000.
- 125. Nakamura, M., Suzuki, T., Amano, K. I., and Yamada, S. Relation of sorption behavior of agricultural chemicals in solid-phase extraction with their n-octanol/water partition coefficients evaluated by high-performance liquid chromatography (HPLC). *Analytical Chimica Acta* 428:219–226, 2001.
- 126. Bielicka, K., and Voelkel, A. Selectivity of solid-phase extraction phases in the determination of biodegradation products. *Journal of Chromatography A* 918:145–151, 2001.
- 127. Masqué, N., Marcé, R. M., and Borrull, F. Molecularly imprinted polymers: New tailor-made materials for selective solid-phase extraction. *TrAC Trends in Analytical Chemistry* 20:477–486, 2001.
- 128. Chuang, J. C., Hart, K., Chang, J. S., Boman, L. E., Van Emon, J. M., and Reed, A. W. Evaluation of analytical methods for determining pesticides in baby foods and adult duplicate-diet samples. *Analytica Chemica Acta* 444:87–95, 2001.
- López, R., Aznar, M., Cacho, J., and Ferreira, V. Determination of minor and trace volatile compounds in wine by solid-phase extraction and gas chromatography with mass spectrometric detection. *Journal of Chromatography A* 966:167–177, 2002.
- 130. Arthur, C. L., and Pawliszyn, J. Solid-phase microextraction with thermal desorption using fused silica optical fibers. *Analutical Chemistry* 62:2145–2148, 1990.
- Arthur, C. L., Potter, D. W., Buchholz, K. D., Motlagh, S., and Pawliszyn, J. Solid-phase microextraction for the direct analysis of water: Theory and practice. *LC-GC* 10:656–661, 1992.
- 132. Yang, X., and Peppard, T. Solid-phase microextraction for flavor analysis. *Journal of Agricultural and Food Chemistry* 42:1925–1930, 1994.

#### 94 FUNCTIONAL POLYMERS IN FOOD SCIENCE

- 133. Penton, Z. E. Sample preparation for gas chromatography with solidphase extraction and solid-phase microextraction: A review. *Advances in Chromatography* 37:205–236, 1997.
- 134. Song, J., Fan, L., and Beaudry, R. M. Application of solid-phase microextraction and gas chromatography/time-of flight mass spectrometry for rapid analysis of flavor volatiles in tomato and strawberry fruits. *Journal of Agricultural and Food Chemistry* 46:3721–3726, 1998.
- 135. Ng, L. K., Hupe, M., Harnois, J., and Moccia, D. Characterization of commercial vodkas by solid-phase microextraction and gas chromatography/ mass spectrometry analysis. *Journal of the Science of Food and Agriculture* 70:380–388, 1996.
- 136. Zhang, Z. Y., and Pawliszyn, J. Headspace solid-phase microextraction. *Analytical Chemistry* 65:1843–1852, 1993.
- 137. Picó, Y., Font, G., Moltó, J. C., and Mañes, J. Solid-phase extraction of quaternary ammonium herbicides: Review. *Journal of Chromatography A* 885:251– 271, 2000.
- 138. Song, J., Gardner, B. D., Holland, J. F., and Beaudry, R. M. Rapid analysis of volatile flavor compounds in apple fruit using SPME and GC/time-of-flight mass spectrometry. *Journal of Agricultural and Food Chemistry* 45:1801– 1807, 1997.
- 139. Jia, M., Zhang, Q. H., and Min, D. B. Optimization of solid-phase microextraction analysis for headspace flavor compounds of orange juice. *Journal of Agricultural and Food Chemistry* 46:2744–2747, 1998.
- 140. Linssen, J. P. H., Janssents, J. L. G. M., Reitsma, J. C. E., and Roozen, J. P. Taste recognition threshold concentrations of styrene in foods and food models. In *Foods and Packaging Materials-Chemical Interactions*, ed. P. Ackermann, M. Jãgerstad, and T. Ohlsson, pp. 74–82. Cambridge: The Royal Society of Chemistry, 1995.
- 141. Morano, J. Isolation and identification of compounds producing adverse flavour effects in packaged food systems. M. S. thesis Rutgers University, New Brunswick, 1974.
- 142. Fernandes, M. H., Gilbert, S. G., Paik, S. W., and Stier, E. F. Study of the degradation products formed during extrusion lamination of an ionomer. *Journal of Food Science* 51:722–725, 1986.
- 143. Risch, J. S. Isolation and identification of migrants from polyester trys: Regulatory and flavour concerns. Ph. D. thesis, University of Minnesota, St. Paul, 1987.
- 144. Powers, J. J. Techniques of analysis of flavours: Integration of sensory and instrumental methods. In *Food Flavour*, ed. III. D. Morton, and A. J. Maclead, pp. 121–168, New York: Elsevier Scientific, 1982.
- 145. Wiley, R. C., Louie, M. K., and Sheu, M. J. Studies on turpentine like offodour in cola. *Journal of Food Science* 49:485–488, 1984.

# Production, Chemistry and Properties of Biopolymers in Food Science

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#### Abstract

It is well known that petroleum derived non degradable synthetic polymer materials have been widely used in every field of human activity during the last decades. In recent years, there has been a clear rise in the interest in use of biodegradable materials in packaging, in various industries. Biodegradable polymers are polymers of natural origin and are long-chain molecules or materials, which have been derived from bio-based monomers. Starches, cellulose, Polylactic acid, Polyhydroxyalkanoates etc., are examples of some of the most commonly used biodegrdable polymers in food packaging. The primary role of packaging is protection and preservation of food from external contamination. This function involves delay of deterioration, extension of shelf life, and maintenance of quality and safety of packaged food. Food packaging is defined as a coordinated industrial and marketing system for enclosing products in a container to meet the following needs: containment, protection, preservation, distribution, identification, communication, and convenience. Biodegradable polymers have the potential to fulfill all these functions without causing any threat to the environment. Most of these polymers can be thermally and physically manipulated to a large extent to have suitable material properties. The suitability of a biomaterial for the purpose of packaging is dependent on its desirable extent of gas barrier properties, water vapor transmittance, thermal and mechanical properties and Compostability. This will also be dependent on cost of production and cost and ease of processing.

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## 4.1 Introduction

Biopolymers are naturally occurring long-chain molecules or materials, which have been derived from biobased monomers [1]. Proteins, enzymes, muscle fibers, polysaccharides and gummy exudates are examples of natural polymers being effectively used in formulating a variety of products. Well-known natural polymers like chitosan, carrageenan, paghula, acacia, agar, gelatine, shellac, guar gum, xanthan gum and gum karaya are widely used in the food industry [1].

On the other hand, biodegradable biopolymers made from annually renewable resources can solve major problems associated with plastics used in the food industry and improve their life cycle by sustainable development. Nowadays biopolymers have emerged as potential alternatives, some of which are available commercially while others are being investigated by researchers. According to the European Technology Platform for Sustainable Chemistry, up to 30 percent of raw materials for the European chemical industry could come from renewable sources by 2025 [2]. As far as the polymer market is concerned, bioplastics are nowadays the fastest growing biobased product globally. But like other biobased innovations they have struggled to achieve a market share, contributing only less than 0.5% of world plastics consumption [3]. Table 4.1 outlines the three most common routes to bioplastics manufacturing and Table 4.2 gives a comparison of major companies in the field [4].

Germany's Nova-Institute is publishing the most comprehensive market study of biobased polymers that has looked at every kind of biobased polymer produced by 247 companies at 363 locations around the world, and they have examined in detail 114 companies in 135 locations [5].

The 3.5 million tonnes in the Figure 4.1 represents a share of 1.5% of an overall polymer production of 235 million tonnes in 2011. Current producers of biobased polymers estimate that production capacity will reach nearly 12 million tonnes by 2020. With an expected total polymer production of about 400 million tonnes in 2020, the biobased share should increase from 1.5% in 2011 to 3% in 2020, meaning that biobased production capacity will grow faster than overall production (Figure 4.1).

Fields of application for bioplastic materials and products are increasing steadily. Many market segments like packaging, food industry & services,

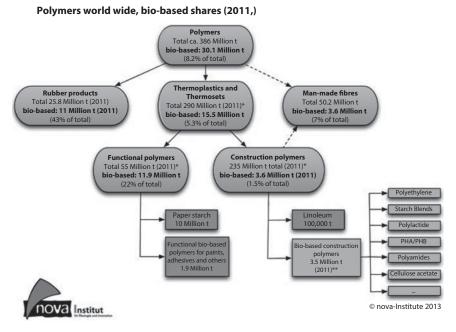
Current methods for biopolymer production	Biopolymers	Examples of marketed biopolymers
Modified natural polymers from plant material	Starch, starch deriva- tives; Cellulose. cellulose derivatives; Lignin	Novamont's starch resin Mater-Bi
Polymers made directly by microorganisms or plants	Polyhydroxyalkanoates, such as Polyhydroxybutyrate and copolymers (PHB/PHAs); Polylactic acid (PLA)	Metabolix. Inc's PHA: Mirel
Polymers made from monomers obtained by fermentation	Polylactic acid (PLA) Polypropylene terephta- late (PPT) Polyethylene (PE) and other ethylene derivatives	Nature Works' PLA DuPont's PPT: Sorona Braskem's Green PE

 Table 4.1 Current methods for biopolymer production [4].

Table 4.2 Comparison	between companies	producing biopolymers [4].
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Company	Polymer	Renewable feedstock	Production technology	Market
BASF	PHAs	Corn	Made by micro- organisms	Niche biodegradable
DuPont	BIO-Propanediol (BIO-PDO)	Corn	Fermentation	Film
Braskem	Green PE	Sugarcane ethanol	Purification of ethanol	Major fibre plastics, Commodity plastics

agriculture/horticultural, consumer electronics, automotive, consumer goods and household appliances are steadily increasing the use of bioplastic materials these days [5]. In food biotechnology, a major proportion of biopolymers serve the purpose of packaging, with the latest development being production of encapsulation systems based on edible biopolymers. Other than these, there are natural polymers that have been used mainly because of their rheological properties.



 (\*): Data from PlasticsEurope 2012. Original data show 45 Million t functional polymers plus 235 Million t construction polymers = 280 Million t total. We added in addition 10 Million t paper starch to the functional polymers -> new total: 290 Million t.
 (\*\*): nova-Institute 2013.

plus Different additional sources.

Figure 4.1 Market share of biopolymers [5].

#### 4.1.1 Examples of Natural Edible Polymers in the Food Industry

Xanthan gum is produced by a pure-culture fermentation of a carbohydrate with *Xanthomonas campestris* and purified. It is also known as Corn sugar gum and is used as a stabilizer, thickener and emulsifier in the food industry for dairy products. Carrageenan is the hydrocolloid obtained from red seaweeds by extraction with water or aqueous alkali and recovered by alcoholic precipitation, drum drying or freezing. Carrageenan is used as a suspending and gelling agent. In the food industry, it is utilized in milk products, ice creams, chocolates, jams and gels in the concentration of 0.5–1% [6].

Cassia gum is a food additive made from the endosperm of *Cassia* obtusifolia, also known as *Senna obtusifolia* or *Cassia tora*. Cassia gum is a naturally occurring polymer with mannose and galactose as its repeating units. Cassia gum develops high viscosity by swelling in water after it is boiled. Cassia gum is the purified flour from the endosperm of the seeds of *Cassia obtusifolia* and *Cassia tora* which belong to the leguminosae family.

Cassia gum is used as thickener, emulsifier, foam stabilizer, moisture retention agent and texturizing agent in cheese, frozen dairy desserts and mixes, meat products and poultry products [6].

# 4.2 Material Properties of Bioplastics Relevant to Food Packaging

Food packaging is defined as a coordinated industrial and marketing system for enclosing products in a container to meet the following needs: containment, protection, preservation, distribution, identification, communication, and convenience [7]. Some of the important functions of a good packaging material are protection and preservation [8]. We will first outline the essential properties required by a good packaging material in order to fulfil the above-mentioned functions. Based on these properties, we will discuss the extent to which the different bioplastics form suitable food packaging materials.

## 4.2.1 Gas Barrier Properties

Many foods require specific atmospheric conditions to sustain their freshness and overall quality during storage. In most packaging applications, the gas mixture inside the package contains carbon dioxide, oxygen, nitrogen or combinations thereof [9]. Literature reports that the presence of just 20% oxygen in the packaging atmosphere is enough to cause the growth of microorganisms and carry out undesirable oxidation of the food [10].

In general, permeability ratios for nitrogen, oxygen and carbon dioxide through polymers are 1:4:14. Oxygen permeability is usually used as a reference while measuring gas barrier properties [11]. These have also been reported to be influenced by humidity in the case of biomass-based bioplastics (those involving cellulose and starch). The gas barrier properties of PLA and PHA are relatively independent of humidity [9].

Thus, food packaging materials must evolve in design to include gas barriers that are able to contain and maintain an optimum combination of gases to preserve the long-term quality of food material.

## 4.2.2 Water Vapor Transmittance

Moisture content control forms an imperative part of food packaging. In some cases, increased moisture content causes food deterioration, while in

other cases loss of moisture is the cause of decline of the food's organoleptic desirability [12].

The presence of moisture is attributed to enabling unnecessary chemical reactions and encouraging growth of unwanted microorganisms [13]. As mentioned in the previous paragraph, loss of moisture particularly affects the texture and appearance of the foodstuff. Changes in relative humidity (RH) cause surface moisture which results in many displeasing textural defects such as lumping, caking, mottling, crystallization and stickiness. The increase in moisture content within the packaging may also occur due to the food; for example, vegetables and other plant tissues give off moisture while respiring during a process called transpiration [6].

The availability of moisture within a food package is measured as water activity. Water activity is measured on a scale of 0 to 1, where 0 indicates no water and 1 indicates all water. Food spoilage microorganisms, in general, are inhibited in food where the water activity is below 0.6. However, if the pH of the food is less than 4.6, microorganisms are inhibited when the water activity is below 0.85 [14].

Thus, it is imperative for the food packaging materials to ensure a rate of water vapor transmittance to keep the water activity level optimum for preservation depending upon the food item.

### 4.2.3 Thermal and Mechanical Properties

Bioplastics are usually semicrystalline in nature; hence exhibit both a glass transition temperature and a melting temperature [13]. Crystalline and glassy regions in a polymer provide barriers to permeants, and a material is usually more permeable above its glass transition temperature due to the decrease in glassy regions [15]. Therefore, knowledge of the Tg and Tm of a polymer is essential for designing good food films with the desired barrier properties.

Some foods (for example, fresh fruits, eggs, biscuits, etc.) are easily damaged and require a higher level of protection from a package. The suitability of a package to protect food from mechanical damage depends on its ability to withstand "crushing" caused by stacking in warehouses or vehicles, "abrasion" caused by rubbing against equipment or during handling, "puncturing" or "fracturing" caused by impacts during handling or by vibration during transport [16]. The mechanical strength of any material is measured by the tensile strength and Young's modulus. While tensile strength gives the measure of how much deformation or tension a material can withstand, Young's modulus is a measure of the material's stiffness or elasticity [13].

## 4.2.4 Compostability

As per the ASTM D 6002, the word "compostable" has been defined as "that which is capable of undergoing biological decomposition in a compost site such that the material is not visually distinguishable and breaks down into carbon dioxide, water, inorganic compounds and biomass at a rate consistent with known compostable materials" [14].

A frequent question that arises out of using bioplastics is the extent of its biodegradability and how long it takes for a bioplastic object to degrade once it reaches the landfill. This is usually a cause for concern as, until they degrade, the bioplastics would be taking up the same amount of space in landfills that traditional plastics do [17].

# 4.3 Materials

## 4.3.1 Starch

#### 4.3.1.1 Production

Starch is a widely available and easily biodegradable natural resource. To produce a plastic-like starch-based film, high water content or plasticizers (glycerol, sorbitol) are necessary. These plasticized materials (with the application of thermal and mechanical energy) are called thermoplastic starch (TPS) and constitute an alternative for polystyrene (PS). Starch-based thermoplastic materials (e.g., blends of TPS with synthetic/biode-gradable polymer) components, like polycaprolactone, polyethylene-vinyl alcohol or polyvinyl alcohol, have been successfully applied on an industrial level for foaming, film blowing, injection molding, blow molding and extrusion applications [18]. Figure 4.2 illustrates various conversion techniques and modifications of starch.

Industrial starch production uses many different extraction techniques. In principle, they are differentiated by the origin of the raw materials. There are cereal starches, root starches, and tuber starches. The processing of supplied raw materials starts with a cleaning step. After that, the material is crushed and then the components are separated by various physical means. Then the separated starch passes on to one more cleaning step and finally it is dehydrated and dried. Well-conducted steeping is an important prerequisite for high yield and good starch quality. This step is conducted at 50°C and lasts about 40 to 50 hours. Steepwater is kept at pH 4 by addition of sulphuric acid or hydrochloric acid and treated with sulphur dioxide. These conditions guarantee optimal water absorption of the maize

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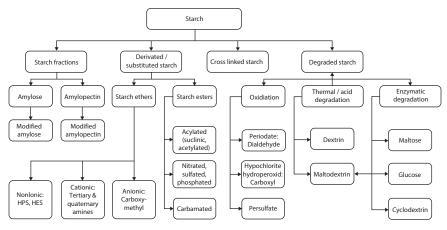


Figure 4.2 Starch conversion techniques and modifications [19].

kernel, controlled fermentation by lactic acid bacteria and loosening of the protein matrix. Growth of lactic acid bacteria suppresses unwanted microorganisms such as yeasts, molds and other bacteria. To free the germs the kernels are coarsely ground in an attrition mill. Separation of specifically lighter germs is conducted by means of special hydrocyclones. Afterwards the germs are washed and dried and finally sold to companies, which utilize them for corn oil production. The germ removal step is followed by fine grinding in an impact mill to completely disrupt the cells of the endosperm and release the starch granules. The resulting suspension is led over bend green cascades for separation from fiber and other maize components. The starch milk, which contains the protein fraction, the so-called gluten, passes through. The bend screen cascades are connected in series. For complete washing out of the starch and separation of the fibers they are operated by the counter flow principle. Additionally, washing water is added to the last process stage. The crude starch milk still contains all the dissolved proteins. This fraction is called gluten, and most of it is separated off by means of two successive nozzle-type continuous centrifugal separators. The process utilizes density differences between starch and protein. The protein fraction is dehydrated by means of a rotary drum filter, then dried and used as a high protein feed additive. The starch milk, which still contains approximately 2% of protein and fibers after separation, is then refined in a multi-step cyclone plant. By optimal construction and adjustment of the plant it is possible to reduce the protein content in the starch below 0.3% on dry matter. The refined starch milk, having a water content of approximately 65%, is dehydrated in peeler centrifuges to a residual water content of about 40%. The inner layer of the filter cake is colored

yellow and contains high amounts of protein. It is reintroduced into the process. Pure starch is finally dried by means of a flash dryer. For optimal shelf life, residual moisture must not exceed 14% [18,19].

The production of starch derivatives is carried out by conversion of native starch with the respective chemicals. Starch conversion is achieved by four different methods: slurry process (aqueous solution), paste reactions, extrusion and semi-dry process, as shown in Figure 4.2 [19].

Modifications give starch its specific and desired properties. Derivatization technologies aim for modifications of the natural starch properties or for the establishment of new ones for utilization of starch in different applications. Thus starch molecules are degraded, chemically modified by introduction of functional groups or changed by hydrothermal technology (Figure 4.3). Starch and modified starches have a broad range of applications in the food sectors like beverages, syrups, deserts, confectionary, bakery products, puddings, gravy, creams and instant meals [19,20].

To achieve other properties and improve cost competitiveness of completely degradable polyesters, their blending with low cost starch is being investigated. Usually, the components to blend with starch are aliphatic polyesters, polyvinyl alcohol (PVA) and biopolymers. The commonly used polyesters are poly(3-hydroxyalkanoates) (PHA), obtained by microbial synthesis, and polyactide (PLA) or polycaprolactone (PCL), derived from chemical polymerization [21,22,23]. Natural polymers such as chitosan,

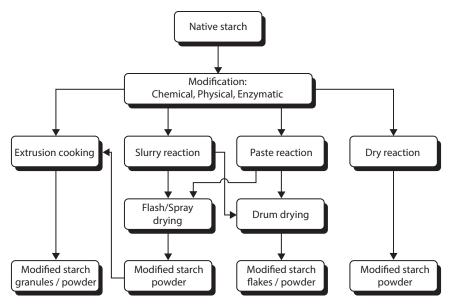


Figure 4.3 Production of starch derivatives [19].

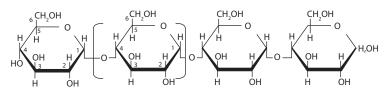
cellulose and their derivatives are studied because the blend exhibits good film-forming properties [21,24]. Extrusion of the mixture of corn starch and microcrystalline cellulose in the presence or absence of plasticizers (polyols) is used to produce edible films [23]. Starch-based nanocomposite films have been obtained by casting the mixture of plasticized starch and flax cellulose nanocrystals.

Food packaging and edible films are two major applications of the starch-based biodegradable polymers in the food industry. Evidently, the starch-based biodegradable polymers are attractive for the food industry and will make great progress in the future.

#### 4.3.1.2 Chemistry and Structure of Starch

Starch granules are composed of two types of alpha-glucan, amylose and amylopectin, which represent approximately 98–99% of the dry weight. The ratio of the two polysaccharides varies according to the botanical origin of the starch. The "waxy" starches contain less than 15% amylose, "normal" 20–35% and "high" (amylo-) amylose starches greater than about 40%. The structure of the alpha-glucans is discussed below in more detail. The moisture content of air-equilibrated starches ranges from about 10–12% (cereal) to about 14–18% (some roots and tubers).

Cereal starches contain integral lipids in the form of lysophospholipids (LPL) and free fatty acids (FFA), which are positively correlated with the amylose fraction, and the LPL may account for up to ~2% of starch weight (in high amylose cereal starches). However, the granules may also be contaminated with surface lipids [29]. The contaminants comprise triglycerides, glycolipids, phospholipids and free fatty acids derived from the amyloplast membrane and non-starch sources. These differ from integral (internal) lipids, which are composed exclusively of the FFAs and LPL [29]. Starches from the Triticeae starches contain almost exclusively LPLs (-choline, -ethanolamine and -glycerol), while other cereal starches are rich in FFAs. Part of the amylose fraction within lipid-containing granules exists as an amylose inclusion complex where the fatty acid chains occupy a hydrophobic core located within the single amylose helix. The presence of these complexes in native starch granules is apparent from <sup>13</sup>C cross polarization-magic-angle spinning/nuclear magnetic resonance (13C CP-MAS/ NMR) [27]. The presence of this fraction is also evident from iodine binding studies where non-defatted amylose from cereal starches has a lower iodine binding capacity than the corresponding lipid-extracted material. The amount of lipid-complexed amylose ranges from <15 to >55% of the



Amylose:  $\alpha$ -(1 $\rightarrow$ 4)-glucan; average n = ca. 1000. The linear molecule may carry a few occasional moderately long chains linked  $\alpha$ -(1 $\rightarrow$ 6).

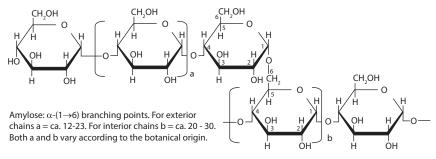


Figure 4.4 Structure of amylose and amylopectin [26].

amylose fraction in cereal starches, with oat starches being especially rich in lipids and correspondingly complexed amylose [27].

#### 4.3.1.3 Biosynthesis of Starch

Starch biosynthesis is a complex process. Sucrose (derived from photosynthesis) is the starting point for alpha-glucan deposition. In the cell cytosol the sucrose is converted to uridine diphosphate glucose (UDP-glucose) and fructose by sucrose synthase, the UDP-glucose being subsequently converted to glucose-1-phosphate (G-1-P) in the presence of pyrophosphate (PPi) by UDP-glucose pyrophosphorylase. This is then itself converted to glucose-6-phosphate (G-6-P) by phosphoglucomutase. The G-6-P is translocated across the amyloplast (the intracellular organelle responsible for starch biosynthesis in storage tissues) membrane by specific translocators and is converted to G-1-P by phosphoglucomutase. There is some evidence that, in cereals at least, G-1-P may be translocated directly into the amyloplast or converted to, and translocated as, adenosine diphosphate glucose (ADP-glucose) generated as a consequence of cytosol-based adenosine diphosphate (ADP)-glucose pyrophosphorylase activity in the presence of adenosine triphosphate (ATP). Using amyloplast located ADP-glucose pyrophosphorylase, G-1-P within the amyloplast is (also) converted to ADP-glucose and provides glucose residues for amylose and amylopectin biosynthesis. Starch synthases (of which there are commonly considered to be two major classes, "granule bound" and "soluble," with a number of isoforms of each) add glucose units to the non-reducing ends of amylose and amylopectin molecules. Granule bound starch synthase can elongate malto-oligosaccharides to form amylose and is considered to be responsible for the synthesis of this polymer. Soluble starch synthase is considered to be responsible for the synthesis of unit chains of amylopectin. Starch branching enzyme creates branching in amylopectin by linking linear chains (branches) to the growing amylopectin molecule.

Starch granules are synthesized in a broad array of plant tissues and within many plant species. Variations in granule size (~1–100  $\mu$ m in diameter), shape (round, lenticular, polygonal), size distribution (uni- or bimodal), association as individual (simple) or granule clusters (compound) and composition ( $\alpha$ -glucan, lipid, moisture, protein and mineral content) reflect the origin of the starch. Although a broad variation of starch granule dimensions and size distributions are available naturally, a selection of plant mutants provide a broader compositional variation and, more recently, transgenic technology achieves a similar objective but in a more controlled fashion. In addition, starches may be chemically, enzymatically or physically modified to induce novel characteristics [27].

## 4.3.1.4 Properties of Starch-Based Bioplastics

### Gas Barrier Properties

Of all starch-based bioplastics, it is the thermoplastic starch that is mostly commercially available. The nontransparent films of this material provide an oxygen permeability of  $815.0 \text{ cc/m}^2/\text{day}$ , which is not permissible for application as a packaging material [28].

### Water Vapor Transmittance

The hydrophilic nature of starch attributes a water vapor transmission rate of 216.4 g/m<sup>2</sup> d to the thermoplastic starch after final formulation. Such values prevent widespread usage of the material in most conventional food packaging applications, while application of thermoplastic starch as edible food packaging material is being explored as a viable option [28].

### Thermal and Mechanical Properties

The glass transition temperature of thermoplastic starch is found to lie in the range of  $-56^{\circ}$ C to  $10^{\circ}$ C. With appropriate coatings like silicon dioxide, the glass transition temperature can be made to occupy a wider range of temperatures to enable cold storage applications by the polymer [10].

The mechanical strength of the thermoplastic starch, measured by a Young's modulus of approximately 650 MPa, is quite low. Thus, this polymer needs much modification before it can be applied as a good food packaging material [28].

#### Compostability

Thermoplastic starch has been found to be highly biodegradable with the pure form of the films being able to completely degrade within 18–20 days. It has been reported that enhanced thermoplastic starch films require up to 45 days to fully decompose, including mineralization of the extra material used for enhancement [28].

## 4.3.2 Cellulose

Cellulose is a fibrous, tough, water-insoluble substance, which is found in the protective cell walls of plants, particularly in stalks, stems, trunks and all woody portions of plant tissues. Cellulose is the most widely spread natural polymer and is derived by a delignification from wood pulp or cotton linters. It is a biodegradable polysaccharide which can be dissolved in a mixture of sodium hydroxide and carbon disulphide to obtain cellulose xanthate and then recast into an acid solution (sulfuric acid) to make a cellophane film. Alternatively, cellulose derivatives can be produced by derivatization of cellulose from the solvated state, via esterification or etherification of hydroxyl groups. Especially these cellulose derivatives were the subject of recent research. Cellulose esters like cellulose (di)acetate and cellulose (tri) acetate need additives to produce thermoplastic materials. Most of them can be processed by injection molding or extrusion. Cellulose ethers like hydroxypropyl cellulose and methyl cellulose are water soluble, except for ethyl cellulose and benzyl cellulose. Ethyl cellulose can be used for extrusion, laminating or molding after addition of plasticizers or other polymers. Most of these derivatives show excellent film-forming properties, but are too expensive for bulk use [30].

### 4.3.2.1 Chemistry and Structure of Cellulose

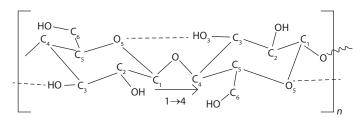
Cellulose is a linear polymer of  $\beta$ -(1->4)-D-glucopyranose units in  ${}^{4}C_{1}$  conformation. The fully equatorial conformation of  $\beta$ -linked glucopyranose residues stabilizes the chair structure, minimizing its flexibility (for example, relative to the slightly more flexible  $\alpha$ -linked glucopyranose residues in amylose). Cellulose preparations may contain trace amounts (~0.3%) of arabinoxylans [6].

Cellulose is an insoluble molecule consisting of between 2000–14000 residues. It forms crystals (cellulose  $I\alpha$ ) where intramolecular (O3-H->O5'

and O6->H-O2') and intrastrand (O6-H->O3') hydrogen bonds hold the network flat, allowing the more hydrophobic ribbon faces to stack. Weak C6-H->O2' hydrogen bonds may also make some contribution to the crystal stability. Each residue is oriented 180° to the next with the chain synthesized two residues at a time. Although individual strands of cellulose are intrinsically no less hydrophilic, or no more hydrophobic, than some other soluble polysaccharides (such as amylose) this tendency to form crystals utilizing extensive hydrophobic interactions [32] in addition to intra- and intermolecular hydrogen bonding makes it completely insoluble in normal aqueous solutions (although it is soluble in more exotic solvents such as aqueous N-methylmorpholine-N-oxide) [32]. It is thought that water molecules catalyze the formation of the natural cellulose crystals by helping to align the chains through hydrogen-bonded bridges.

## 4.3.2.2 Biosynthesis of Cellulose

To date, bacterial cellulose is rather unexploited, but it represents a polymeric material with major potential. Bacterial strains of *Acetobacter xylinum* and *A. pasteurianus* are able to produce an almost pure form of cellulose (homo-beta-1,4-glucan). Its chemical and physical structure is identical to the cellulose formed in plants. Plant cellulose, however, has to undergo a harsh chemical treatment to remove lignin, hemicellulose and pectins. This treatment severely impairs the material characteristics of plant cellulose; the degree of polymerization decreases almost tenfold and the form of crystallization changes. Bacterial cellulose is processed under ambient conditions and the degree of polymerization is 15000, 15 times longer than cellulose, 70% is in the form of cellulose I and the rest is amorphous. This composition results in outstanding material properties; a modulus as high as 15–30 GPa was determined across the plane of the film. Production costs of bacterial cellulose are high due to the low efficiency of the bacterial



**Figure 4.5** Single cellulose chain repeat unit showing the directionality of the  $1 \rightarrow 4$  linkage and intrachain hydrogen bonding (dashed lines) [31].

process; approximately 10% of the glucose used in the process is incorporated in the cellulose. The high price of bacterial cellulose of approximately 20 Euro/kg hampers its applicability in low-added-value bulk products. Several high-added-value specialty applications have been developed. The material has been used as an artificial skin, as a food-grade nondigestible fiber, as an acoustic membrane, and as a separation membrane [32].

## 4.3.2.3 Properties of Cellulosic Bioplastics

The cellulose-based films available in the market include cellulose, cellulose acetate and its derivatives [33]. The physical properties of these bioplastics enabling them to be suitable food packaging materials are mentioned below in detail.

#### Gas Barrier Properties

In almost all cases, depending on the type of auxiliary coatings provided, the gas barrier properties can be enhanced to a certain degree to be comparable to the current synthetic favorites. Transparent cellophane has been reported to display low levels of oxygen permeability of 9.9cc/m<sup>2</sup> d, while nontransparent films are even more impermeable to oxygen at 3.4cc/m<sup>2</sup> d. This makes cellulose-based bioplastics highly suited for packaging of food items requiring long shelf life [28].

### Water Vapor Transmittance

It has been found that the production process as well as enhancement processes can improve the water vapor transmission rates of cellulose-based films to values of  $10.1 \text{ g/m}^2 \text{ d}$ , which are comparable to conventional plastics. However, these materials cannot be used as higher water vapor barriers [28].

### Thermal and Mechanical Properties

Cellulose-based bioplastics are greatly semicrystalline in nature, thus exhibiting a melting temperature ( $T_m$ ) of around 170°C. The glass transition temperature ( $T_g$ ) of cellulose diacetate is reported to lie in the range of 110–140°C [34]. Thus, these bioplastics provide a wide-range of temperature protection to the foods enclosed in them.

Cellulose-based bioplastics exhibit a tensile strength greater than 3000 Mpa, making them at par with conventional plastics in material strength. Thus, these can easily be used for protecting food requiring special mechanical protection [28].

### Compostability

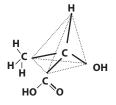
Any cellulose-derived bioplastic is completely biodegradable. When buried, uncoated cellophane degrades in 28-60 days and coated cellophane degrades in 80–120 days. However, the biodegradability of cellulose acetate varies with degree of substitution [34].

## 4.3.3 Polylactic Acids (PLAs)

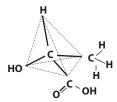
## 4.3.3.1 Production of PLAs

PLA (polylactic acid) is a family of biodegradable thermoplastic polyesters made from renewable resources which is currently one of the most favorable polymers for commercial use as a substitute for polyethylene, polystyrene (PS) and polyethyleneterephthalate (PET). Lactic acid, the monomer of polylactic acid (PLA), may easily be produced by fermentation of carbohydrate feedstock. The carbohydrate feedstock may be agricultural products such as maize and wheat, or alternatively may consist of waste products from agriculture or the food industry, such as molasses and whey [35]. The PLA pellets are obtained through direct polycondensation of lactic acid monomers or through ring-opening polymerization of lactide. Since lactic acid exists as two optical isomers, L- and D-lactic acid, three different stereochemical compositions of lactide can be found, i.e., L,L-lactide, D,Dlactide and L,D-lactide. This stereochemical composition determines the final properties of the polymer. The processing possibilities of this transparent material are very wide, ranging from injection molding and extrusion over cast film extrusion to blow molding and thermoforming [18].

Polylactic acid is the most common bioplastic in use today. Twenty-five companies have developed production capacity at 30 sites worldwide of over 180,000 tons of PLA [36]. The largest producer is NatureWorks, a company that is active in the USA and Thailand, and has a capacity of 140,000 t/year. The other producers have a current capacity of between 1,500 and 10,000 t/year. According to the forecasts, existing PLA producers are planning considerable expansion of their capacity to around 800,000 t/year by 2020. There should be at least 7 sites with a capacity of over 50,000 t/year



L (levo, +, S) lactic acid



D (dextro, -, R) lactic acid

Figure 4.6 Optical isomers of lactic acid [46].

by then. A survey of lactic acid producers—the preliminary stage of PLA production—revealed that production capacity to meet concrete requests from customers could even rise to roughly 950,000 t/year [36].

Another producer is the Netherlands-based Synbra Technology, which started its 5,000 tonnes/year PLA plant in Allschwil (Switzerland) in 2011, which also plans to expand its capacity to 50,000 tonnes/year [35]. Other major companies involved in PLA manufacturing are Toyobo, Dai Nippon Printing Co., Mitsui Chemicals, Shimadzu, NEC and Toyota (Japan), PURAC Biomaterials and Hycail (The Netherlands), Galactic (Belgium), Cereplast (USA), FkuR, Biomer, Stanelco and Inventa-Fischer (Germany), and Snamprogetti (China) [37,38].

Sulzer Chemtech now offers a complete plant solution for a PLA polymerization process which was jointly developed with Purac. The basis for PLA production with the Sulzer process is lactide polymerization in a continuous, fully integrated process using Sulzer Chemtech's proprietary SMR technology and equipment. Sulzer Chemtech has developed a new generation of reactors based on the principle of static mixing and on continuous bulk polymerization, e.g., mass and solution polymerization. This reactor is characterized by accurate control of heat transfer and mixing effects so that high conversion and consistently high polymer quality are achieved reproducibly in order to meet varied and stringent requirements. This state-ofthe-art PLA production technology has advantages compared to standard technologies like: very efficient polymerization process using static mixer technology; short time requirement to switch to a different PLA grade due to low residence times; operational flexibility to produce different PLA grades with different molecular weights; straightforward scalability to bigger plant sizes; and low maintenance costs due to the installation of mainly static equipment. Since 2012, Sulzer Chemtech has had their own 1000 t/yr PLA production unit. Sulzer PLA is characterized by its high optical purity, its low level of residual monomer and a wide range of accessible molecular weights. Due to an extremely low level of racemization, Sulzer's PLA process gives access to either pure PLLA or PDLA, exhibiting very high degrees of crystallinity, or to PDLLA copolymers with precisely adjusted L/D-ratios. Their yellowness index and polymer stability (avoiding monomer reformation during processing) are among the best in the market. The PLLA and PDLA may also be compounded to stereocomplex PLA (scPLA), exhibiting outstanding temperature stability (>180°C HDT-B) [39,40].

Considerable efforts have been made to improve the properties of PLA so as to compete with low-cost and flexible commodity polymers. These attempts were carried out either by modifying PLA with biocompatible plasticizers or by blending PLA with other polymers [30,41]. Such multilayer

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films or sheets can be formulated into several different types of packaging shapes such as bags, pouches, plates, cups, trays, and clamshells for various types of food materials including retail packaging for meats, cheese, confectionery, as well as fresh fruits and vegetables. The mechanical and barrier properties of these films are enhanced by various physical, chemical, or enzymatic treatments, as well as blending with hydrophobic additives, or making multilayer films with different film properties [30,41,42]. Multilayer films formed through coating or lamination methods have been widely used to combine the properties of two or more polymers into one single multilayered structure [43]. Also, in this case, the use of nanometric filler promises to further expand its application. Polylactic acid has been used for the preparation of polymer/clay nanocomposite materials, e.g., with montmorillonite (MMT) [44]. Solvent casting of mixtures of PLA and organophilic clay in chloroform resulted in materials with an enhanced crystallization tendency and increased Young's modulus [45]. Also, PLA/ layered silicate nanocomposites, prepared by simple melt extrusion, exhibited remarkable improvement of material properties in both solid and melt states compared to the matrix without clay [45].

#### 4.3.3.2 Chemistry and Synthesis of PLAs

Lactic acid exists as two optical isomers, L- and D-lactic acid.

Two optically active configurations of PLA, the L(+) and D(-) stereoisomers, are produced by bacterial (homofermentative, resulting principally in a single end product, and heterofermentative, resulting in a number of end products) fermentation of carbohydrates. First, corn or other raw materials are fermented to produce lactic acid, which is then polymerized to make polylactic acid (PLA) [38,39].

The homofermentative method using corn starch or cane sugar is preferred for industrial production because it leads to greater yields of lactic acid and to lower levels of byproducts. However, lactic acid cannot be directly polymerized to a useful product, owing to the generation of water which degrades the forming polymer. Instead, it is dimerized to lactide and PLA of high molecular weight is produced from the lactide by ring-opening polymerization. This mechanism does not generate additional water, and hence, a wide range of molecular weights are accessible. Typically PLA has a number average molecular weight ( $M_n$ ) between 75000 and 100000 Daltons [39].

A number of microbes are capable of producing lactic acid by aerobic and anaerobic fermentation processes. *Lactobacillus* species are currently used extensively in industry for starch-based lactic acid production. The majority of these species lack the ability to ferment pentose sugars such as xylose and arabinose. Although *Lactobacillus pentosus*, *Lactobacillus brevis* and *Lactococcus lactis* are able to ferment pentoses to lactic acid, pentoses are metabolized using the phosphoketolase pathway, which is inefficient for lactic acid production. Other processes consist of using species such as *Lactobacillus delbrueckii*, *L. amylophilus*, *L. bulgaricus*, and *L. leichmanii*, at a pH range of 5.4 to 6.4, temperature range of 38 to 42°C, and a low oxygen concentration. Generally, pure L-lactic acid is used for PLA production [40].

In the phosphoketolase pathway mentioned above, xylulose-5-phosphate is cleaved to glyceraldehyde-3-phosphate and acetyl phosphate. With this pathway, the maximum theoretical yield of lactic acid is limited to one per pentose (0.6 g lactic acid per g xylose) due to the loss of two carbons to acetic acid. In most platform host organisms such as E. coli, production of lactic acid at high titres is either inefficient or toxic. The production of lactic acid at neutral pH typically results in the production of Ca-lactate, which has to be converted into lactic acid by the addition of sulphuric acid, resulting in the formation of CaSO<sub>4</sub> (gypsum) as byproduct. To produce lactic acid directly, the fermentation needs to be carried out at low pH (preferably at least one unit lower than the pK value of lactic acid, 3.85). Lactic acid however is toxic to microorganisms, as in its protonated form it acts as an uncoupler that destroys the membrane potential. Thus, while quite a few microorganisms may be tolerant to low pH, limited numbers of organisms are suitable for organic acid production. Hence, improved methods for PLA production need further investigation.

There are two important methods for PLA synthesis: direct polycondensation of lactic acid and ring-opening polymerization of lactic acid cyclic dimer, known as lactide. Figure 4.7 shows the reaction mechanism for both of them. In direct condensation, solvent is used and higher reaction times are required. The resulting polymer is a material of low to intermediate molecular weight.

In direct condensation, solvent is used under high vacuum and temperatures for the removal of water produced in the condensation. This approach was used by Carothers and is still used by Mitsui Chemicals. The resultant polymer is a low to intermediate molecular weight material, which can be used as is, or coupled with isocyantes, epoxides or peroxide to produce a range of molecular weights [47]. In the solvent-free process, a cyclic intermediate dimer, commonly referred to as lactide (Figure 4.7), is produced and purified by distillation. Catalytic ring-opening polymerization of the lactide intermediate results in PLA with controlled molecular weight [48]. By controlling residence time and temperatures in combination with catalyst type and concentration, it is possible to control the ratio and sequence of D- and L-lactic acid units in the final polymer [47].

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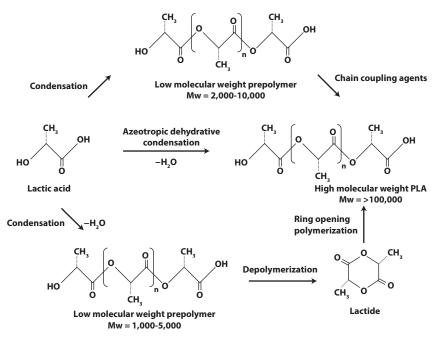


Figure 4.7 Synthesis of Polylactic acid [47].

## 4.3.3.3 Properties of PLA

#### Gas Barrier Properties

Polylactic acid (PLA) is a very widely popular biopolymer in use as a biodegradable food packaging material. It exhibits oxygen permeability of 25.4 cc/m<sup>2</sup>/day making it a competitive material to commercially available conventional plastics [28].

#### Water Vapor Transmittance

PLA provides a very high water vapor barrier displaying water vapor transmission rate of 2.3 g/m<sup>2</sup> d. Thus, it is a very suitable material for preserving food materials requiring long-term protection [28].

#### Thermal and Mechanical Properties

PLA is semicrystalline in nature like cellulose-based bioplastics, exhibiting a melting temperature in the range of 200–205°C and a glass transition temperature of 58°C [49]. It has a tensile strength of 2300 MPa. It is comparable to mineral-oil-based plastics as a mechanically strong food packaging material [28].

#### Compostability

While PLA sheets have been reported to not undergo any changes in a natural composting environment, PLA bottles were reported to have undergone complete degradation over a period of 30 days [15]. It is suggested that PLA does not biodegrade readily at temperatures less than 60°C due to its "glass transition" temperature being close to 60°C [49].

## 4.3.4 Polyhydroxyalkanoates (PHAs)

## 4.3.4.1 Production of PHAs

Currently PHAs show the highest growth rates on the market after PLA. The PHA biobased polymers will more than quadruple their capacity between 2011 and 2020 [84]. Many large companies such as Meredian (US), Ecomann (China), and Bio-on (Italy) are focusing on increasing production capacities. A large number of companies, particularly small and middle-sized ones have initiated the experimental and industrial scale manufacturing of all types of PHAs. Biomer, Bio-On SRL, Kaneka Corporation, Metabolix Inc., Newlight Technologies, LIC PHB Industrial S. A., Polyferm Canada Inc., Shenzhen Ecomann Biotechnology Co. Ltd, Tianan Biologic Materials Co. Ltd, and Tianjin GreenBio Materials Co. Ltd. are the companies that are connected with PHA production. Although the existing PHA plant capacities are underutilized at present, the companies are still planning for further capacity expansions. According to the polyhydroxyalkanoates (PHA) producer Meredian, Inc., the largest world plant will produce 30,000 t of PHA per year at the Bainbridge (USA) plant. [50].

The PHAs can be produced using various renewable raw materials. Currently, the majority of PHA is produced using plant sugar, which can be easily obtained from sugarcane, corn sugar, and sugar beet, making it an ideal raw material for PHA [50]. A considerable amount of PHA is also produced using plant or vegetable oils such as soybean oil, palm oil, and corn oil. Waste lipids and milk whey are the other raw materials at experimental stage and can be commercialized soon. Meredian's PHA is produced via fermentation using plant-based fatty acids (unlike its competitors who are focusing on sugar) as feedstock. Meredian actually acquired its PHA technology from Procter & Gamble in 2007 [51].

These PHAs occur as either homopolymers or copolymers. Polyhydroxybutyrate (PHB) is the most common type of PHA; it is produced by a wide range of bacteria. PHA-producing bacteria can be divided into two groups according to the culture conditions required for PHA synthesis. The first group requires the limitation of an essential nutrient (s) for the production of PHAs. Bacteria in this group include *Cupriavidus necator, Rhodopseudomonas palustris* and *Methylobacterium organophilum*. The second group synthesizes PHAs alongside growth in the cultivation medium. Bacteria in this group include *Alcaligenes latus* and recombinant *E. coli* containing the PHA biosynthetic genes [52]. Certain bacteria can accumulate biopolymers such as PHAs up to 90% of the dry cell weight (DCW, w/w). Bacillus spp. are able to utilize a wide range of substrates, such as sugars, volatile fatty acids (VFAs), alcohols, and biowaste materials, to produce homopolymers such as P(3HB). The P(3HB) yields are highly variable among the different Bacillus species: *B. amyloliquefaciens, B. brevis, B. cereus, B. circulans, B. coagulans, B. firmus, B. laterosporus, B. licheniformis, B. macerans, B. megaterium, B. mycoides, B. sphaericus, B. subtilis, B. thuringiensis and Bacillus sp, which is largely due to either the type of strain or feed used in the process [53].* 

Efforts to improve P(3HB) yields were made through mutagenesis via mutagens such as UV, acriflavine, and 5-bromouracil. These resulted in a twofold increase compared to the yields of wild-type strains. The P(3HB) yields of *B. megaterium* Y6, *B. subtilis* K8, and *B. firmus* G2 increased from 48.13%, 32.50%, and 15.62% of DCW to 63.45%, 61.32%, and 34.12% of DCW in their respective mutants [54]. With complex substrates such as nutrient medium, raffinose, and starch, the P(3HB) yields were in the range of 48.1–60.6% of DCW [55,56]. Exceptionally, *Bacillus sp* strain CL1 has been reported to exploit different sugars such as glucose, sucrose, and raffinose, to yield PHA up to 90% of DCW [57]. Hence, it is a highly suitable candidate for use in large-scale production.

In order to develop more cost-effective processes for PHA production several different strategies are being applied. One of them involves the use of microbial mixed cultures (MMC) combined with the utilization of low value substrates as agro-industrial waste and byproducts. This approach allows for lower investment and operating costs for the global process [58]. One of the main problems with these strategies is the low PHA content achieved when compared with the ones reported for pure culture and synthetic substrates. However, recently a similar PHA content (74.6%) using MMC and fermented molasses was obtained [59]. Culture selection with a high PHA storage capacity is one of the challenges in the mixed culture PHA production process.

Cheap carbon sources such as whey, wastewater from olive mills, molasses, corn steep liquor, starchy wastewater and palm oil mill effluent are used to reduce production costs. The use of bio-oil resulting from fast pyrolysis as a possible feedstock to produce short-chain-length polyhydroxyalkanoates, composed of monomers with 4 and 5 carbons (HB and HV), using mixed microbial cultures was also demonstrated [60].

Transgenic plants are also used for low-cost production of PHAs. Producing PHAs in plants, on the other hand, will help connect the lowcost/high-volume sustainable production capacity of crops with the vast number of developing polymer industries and should not promote much controversy. Many research groups have reported their attempts to produce PHAs in plant systems. The overall costs would make PHA production economical. Transgenic plants containing the PHA synthase genes have been created. The transgenic plants were stunted but accumulated about 15% dcw (dry cell weight) of P(3HB) in the leaf expression systems. Copolymers of 3HB and 3HV were produced in Arabidopsis and Brassica rapa. The production of PHAs can take place in plastids or in seeds. Arabidopsis plants accumulated P(3HB) up to 14% of the leaf dry weight. Transgenic PHA-producing plants have also been produced using tobacco, cotton, and flax systems. However, plant systems have other disadvantages. It is difficult to produce copolymers in plant systems since the production is under the control of endogenous metabolic precursors in the plant. Similarly, the recovery of the polymer from plant tissues is a tricky and expensive affair. Monsanto previously produced P(3HB) and P(3HB-co-3HV) in Arabidopsis and Brassica rapa and these polymers resembled the bacterial polymers. Researchers in Japan have also recently devised a transgenic Arabidopsis thaliana, harboring an engineered PHA synthase gene from Pseudomonas sp 3; fabH gene (codes for 3-ketoacyl-ACP synthase III) from E. coli and a phaAB gene (codes for a ketothiolase and acetoacetyl-CoA reductase) from Cupriavidus necator, and the enzymes were targeted to the plastids. A polymer consisting of 3-hydroxybutyrate unit and a small portion of 3-HA units (C5-C14) was produced [61].

#### 4.3.4.2 Chemistry and Structure of PHAs

Polyhydroxyalkanoates (PHAs) (Figure 4.8) are a complex class of polyesters produced by a wide variety of different bacteria and members of the family Halobacteriaceae of the Archaea. They are produced as intracellular storage compounds for carbon and energy, under nutrient-limiting conditions in the presence of excess carbon. Although derived biologically, they resemble certain synthetic absorbable polymers and hence have many potential medical applications.

The PHAs are stored as water-insoluble inclusions in the cytoplasm of bacteria [63]. These granules are produced in bacteria when subjected to an unbalanced growth condition with excess carbon and simultaneous

limitation of nutrients such as oxygen, nitrogen, sulphur, magnesium and phosphorous [63]. However, there are some bacteria like *Alcaligenes latus* that produce PHAs even when not under nutrient constraints [24].

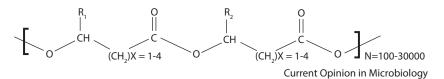
## 4.3.4.2.1 SCL and MCL PHAs

Polyhydroxyalkanoates (PHAs) can have varied monomeric units as shown in Figure 4.8. Based on the number of carbon atoms in the monomeric unit, PHAs can be categorized into short-chain-length (SCL) PHAs containing 3–5 carbon atoms, e.g., poly-3-hydroxybutyrate, P(3HB) and mediumchain-length (MCL) PHAs, containing 6–14 carbon atoms, e.g., poly-3-hydroxyhexanoate (P3HHx) [64]. Copolymers of PHAs are also found and depending on the type of monomeric units present, these could be copolymers of SCL PHAs, e.g., poly(3-hydroxybutyrate-co-3-hydroxyvalerate), P(3HB-co-3HV), copolymers of MCL PHAs such as poly(3-hydroxyhexanoate-co-3-hydroxyoctanoate), P(3HHx-co-3HO) and copolymers of SCL-MCL PHAs, e.g., poly-3-hydroxybutyrate-co-3-hydroxyhexanoate, P(3HB-co-3HX).

Based on the organism used, the culture conditions and the carbon sources provided, the molecular structure of the PHAs can vary. The MCL-PHAs are produced mainly by Gram negative bacteria belonging to the rRNA homology group I such as the genus *Pseudomonas*. *Bacillus sp* such as *B. sphearicus*, *B. subtilis*, *B. megaterium* and *B. cereus* SPV have been extensively studied with regard to the production of P(3HB) and P(3HB-3HV) [63,64]. *Bacillus sp*, e.g., *B. cereus* SPV, use a broad spectrum of substrates ranging from fatty acids, plant oils and carbohydrates to produce P(3HB) and P(3HB-co-3HV).

## 4.3.4.3 Biosynthesis of PHAs

The biosynthesis of PHAs includes two important steps, the first one generates hydroxyacyl-CoA substrates and the second one involves the polymerization of these substrates leading to the formation of the PHAs. Three metabolic pathways (Pathway I: Chain elongation reaction;



**Figure 4.8** The general structure of Polyhydroxyalkanoates (x = 1, 2, 3; n = 100-30000;  $R_1$ ,  $R_2$  = alkyl groups,  $C_1$ - $C_{13}$ ) [62].

Pathway II: Fatty acid ß-oxidation; Pathway III: Fatty acid *de novo* biosynthesis) have been known to be associated with PHA biosynthesis [65].

Pathway I (Figure 4.9) involving the chain elongation reaction is the best known among the PHA biosynthetic pathways [66]. Here, the condensation of two acetyl-CoA molecules from the tricarboxylic acid (TCA) cycle takes place to form acetoacetyl-CoA with the help of the enzyme ß-ketothiolase [66]. Acetoacetyl-CoA is then converted to (R)-3-hydroxybutyryl-CoA by the (R)-specific acetoacetyl-CoA reductase. Finally, the PHA synthase enzyme catalyzes the polymerization via esterification of 3-hydroxybutyryl-CoA into poly (3-hydroxybutyrate), P(3HB).

Pathway II involves the fatty acid ß-oxidation in the presence of substrates such as fatty acids and oils [8] (Figure 4.9). The monomeric composition is related to the carbon sources used [66]. Here, the fatty acids are first converted to the corresponding acyl-CoA thioesters, which are then oxidized by fatty acid ß-oxidation via trans-2-enoyl-CoA and (*S*)-3hydroxyacyl-CoA to form 3-ketoacyl-CoA. The 3-ketoacyl-CoA is then cleaved by a ß-ketothiolase to form acetyl-CoA and an acyl-CoA comprised of two less carbon atoms as compared to the acyl-CoA that entered the first cycle. Subsequent cycles follow until the original acyl-CoA is completely converted to acetyl-CoA.

Pathway III involving fatty acid *de novo* biosynthesis is significant as it helps generate PHA monomers from structurally unrelated carbon sources such as glucose, sucrose and fructose. In this pathway, the enzyme acyl-CoA-ACP transferase (encoded by *phaG*) transfers the hydroxyacyl moiety from (R)-3-hydroxy-acyl carrier protein to coenzyme A, thus forming (R)-3-hydroxyacyl-CoA, which acts as the substrate for the PHA synthase enzyme [66,67].

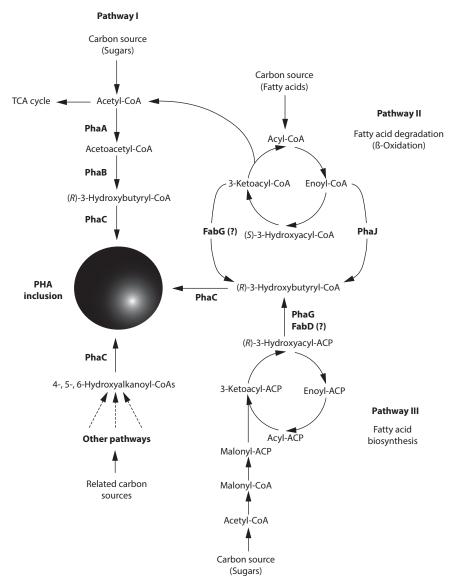
#### 4.3.4.4 Properties of PHAs

#### Gas Barrier Properties

The most widely used PHA is P(3HB) or poly-3-hydroxybutyrate. When applied as a packaging material, P(3HB) exhibits an oxygen permeability of about 142 cc/m<sup>2</sup> d. This can be improved by blending with other biodegradable polymers such as cellophane [28].

#### Water Vapor Transmittance

P(3HB) has a moderately high water vapor transmission rate of 80.6 g/m<sup>2</sup> d. Although P(3HB) in itself may not be applied directly as a high water vapor barrier, composites involving P(3HB) and cellulose-based polymers are good alternatives [28].



**Figure 4.9** Metabolic pathways that supply hydroxyalkanoate monomers for PHA biosynthesis. PhaA, b-ketothiolase; PhaB, NADPH-dependent acetoacetyl-CoA reductase; PhaC, PHA synthase; PhaG, 3-hydroxyacyl-ACP-CoA transferase; PhaJ, (R)-enoyl-CoA hydratase; FabD, malonyl-CoA-ACP transacylase; FabG, 3-ketoacyl-CoA reductase [66].

#### Thermal and Mechanical Properties

P(3HB) exhibits 60–80% crystallinity, and thus has a  $T_m$  of 180°C, and a glass transition temperature of 4°C. This enables the application of this biopolymer for long term storage of food products at and above room temperature [15].

While P(3HB) has a Young's modulus of 3500 MPa, it is a highly brittle polymer with a tensile strength of only 40 MPa. Thus, blending P(3HB) with other malleable biopolymers such as thermoplastic starch or mcl-PHAs can improve its mechanical properties and provide adequate protection to the packaged food items [49].

Compostability

Many bacteria in the soil excrete enzymes that enable degradation of PHAs, including P(3HB). It was found that pure P(3HB) degrades 60–70% of its original weight in 30 days. Thus, over a maximum period of 45–60 days, the P(3HB) product is completely degraded in real composting conditions, i.e., compost containing cow manure, wood shavings, and waste feed.

## 4.4 Future Prospects

The profitability of bioplastics for industry still remains unclear. This is connected with difficulties like scaling up small-scale biotechnologies to industrial level, developing new infrastructures and introducing new unknown products [68]. Despite this, there are many examples of bioplastic production by ASF, DuPont, Braskem, and NatureWorks. Nowadays biobased polymers are produced by 247 companies at 363 locations. The most active areas of biopolymer production involve fermentation in biorefineries that are constructed near crop collection and processing points to avoid the costs of transporting biomass over long distances. The costly separation operation associated with fermentation can be avoided by producing polymer directly in plants cells. Such attempts of genetic engineering of plants are currently under development [69,70].

Biobased polymers PLA and PHAs, which are new in the market, are also expected to at least quadruple their capacity between 2011 and 2020. Most investments in new biobased polymer capacities are predicted to take place in Asia and South America because of better access to feedstock and a favorable political framework. Europe's share will decrease from 20% to 14% and North America's share from 15% to 13%, whereas that of Asia is predicted to increase from 52% to 55% and South America's from 13% to 18% [71]. So, world market shares are not expected to shift dramatically, which means that all parts of the world will experience development in the field of biobased polymer production [5].

Europe's current position in producing biobased polymers is limited to a few polymers. However, some new developments and investments are foreseen: the first European industrial-scale PLA plant is expected to be completed by 2014; the introduction of future PET production facilities is expected to be established by 2015; recent developments in the commercialization of biobased polybutylene terphthalate (PBT) and further advancements in the field of high-value fine chemicals for polyamide (PA), polyurethane (PUR) and thermosets production is predicted. Although Europe shows a strong demand for biobased polymers, production tends to take place elsewhere, namely in Asia and America [5].

Some targets of biopolymers and natural fiber composites in comparison to their conventional counterparts have been specified [72]. They should save at least 20 MJ (non-renewable) energy per kg polymer; avoid at least 1 kg  $CO_2$  emission per kg polymer; and reduce most other environmental impacts by at least 20%. The convergence of a set of strong drivers for the expansion of the bioplastics sector suggests that there is a bright future for both biodegradable and recyclable biobased plastics.

## References

- 1. Song, J. H., Murphy, R. J., Narayan, R., Davies, G. B. H. *Philosophical Transactions of the Royal Society B* 364:2127, 2009.
- 2. Yates, M. R. and Barlow, C. Y. *Resources, Conservation and Recycling* 78:54, 2013.
- 3. Product overview and market projection of emerging bio-based plastics PRO-BIP 2009, Report for European Polysaccharide Network of Excellence (EPNOE) and European Bioplastics 243, Universeitet Utrecht, the Netherlands, 2009.
- 4. Iles, A. and Martin, A. N. Journal of Cleaner Production 45:38, 2013.
- 5. Nova Institute, market study on biobased polymers in the world, http://www. bio-based.eu/market\_study/pressrelease, 2013.
- 6. Suvorova, A. I., Tyukova, I. S., and Trufanova, E. I. *Russian Chemical Reviews* 69:451–459, 2000.
- 7. Robertson, G. L. *Food Packaging: Principles and Practice*. New York: Marcel Dekker, 1993.
- Soroka, W. Fundamentals of Packaging Technology, 2nd ed., Institute of Packaging Professionals, 1999.
- 9. Biobased Packaging Materials for the Food Industry: Status and Perspectives, Royal Veterinary and Agricultural University, Denmark, 2000.

- 10. Cooksey, K. International Journal of Polymer Science, vol. 2012.
- 11. Kit, L., et al. The Wiley Encyclopedia of Packaging Technology. John Wiley & Sons, 2010.
- 12. Siracusa, V., et al. Trends in Food Science & Technology 19:634-643, 2008.
- 13. Smith, J. S., Hui, Y. H., eds. *Food Processing Principles and Applications*. Iowa: Blackwell, 2004.
- Ontario Ministry of Agriculture and Food, Food Processing and Preservation, Ontario, *Canada*, 2013.
- 15. Jamshidia, M., et al. Comprehensive Reviews in Food Science and Food Safety 9:552–571, 2010.
- 16. Fellows, P. *Food Processing Technology: Principles and Practice*, 2nd ed. Cambridge: Woodhead Publishing Ltd, 2000.
- 17. Discovery, What are some examples of bioplastics? http://curiosity.discovery. com/question/what-some-examples-of-bioplastics, 2010.
- 18. Vert, M., Santos, I. D., Ponsart, S., Alauzet, N., Morgat, J. L., Coudance, J., Garreau, H., *Polymer International* 51:840, 2002.
- Grüll, D. R., Jetzinger, F., Kozich, M., Wastyn, M. M. and Wittenberger, R. Industrial starch platform: Status quo of production, modification and application. In *Biorefineries – Industrial Processes and Products: Status Quo and Future Directions*, eds. B. Kamm, P. R. Gruber, and M. Kamm, vol. 2, pp. 61– 95. Wiley-VCH Verlag, 2006.
- 20. Nair, L. S. and Laurencin, C. T. Progress in Polymer Science. 32:762-798, 2007.
- 21. Lu, D. R., Xiao, C. M., Xu, S. J. Express Polymer Letters 3:366, 2009.
- 22. Mani, R. and Bhattacharya, M. European Polymer Journal 37:515, 2001.
- 23. Ratto, J. A., Stenhouse, P. J., Auerbach, M., Mitchell, J., Farrell, R. *Polymer* 40:6777, 1999.
- 24. Doi, Y. Microbial Polyesters, New York, VCH Publishers, 1990.
- 25. Bastioli, C. Global status of the production of biobased packaging materials. *StarchStärke* 53 (8): 351–355, 2001.
- Tester, R. F. Karkalas, J. Starch: Composition, fine structure and architecture. *Journal of Cereal Science* 39 (2): 151–154, 2004.
- 27. Sudesh, K., Abe, H., Doi, Y. Synthesis, structure and properties of polyhydroxyalkanoates: Biological polyesters. *Progress in Polymer Science* 25 (10): 1503–1555, 2000.
- Peelman, N., et al. Application of bioplastics for food packaging. Trends in Food Science and Technology 32:128–141, 2013.
- 29. Bourtoom, T., and Chinnan, M. S. Food Science and Technology 41:1633, 2008.
- Luckachan, G. E. and Pillai, C. K. S. Journal of Polymers and the Environment 19:637, 2011.
- 31. Ali, C., et al. Journal of Nanomaterials, 44, 2013.
- 32. Lindman, B., Karlström, G., and Stigsson, L. *Journal of Molecular Liquids* 156:76-81, 2010.
- Varshney, V. K., Sanjay, N. Cellulose Fibers: Bio-and Nano-Polymer Composites. Heidelberg: Berlin, 2011.

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- 34. Packaging Technology, Cellophane, http://packagingtech.net/60-cellophane. html, 2012.
- Green Chemicals Blog, NatureWorks expands PLA capacity, http://greenchemicalsblog.com/2012/09/06/natureworks-expands-pla-capacity/, 2012.
- Wool, R., and Sun, X. S. *Bio-based Polymers and Composites*, Academic Press, 2011.
- 37. Datta, R., and Henry, M. *Journal of Chemical Technology and Biotechnology* 81:1119, 2006.
- Jamshidian, M., Tehrany, E. A., Imran, M., Jacquot, M., Desobry, S. Comprehensive Reviews in Food Science and Food Safety 9:552, 2010.
- Weusthuis, A. R., Wolbert, E. J. H., Springer, J., and van der Oost, J. Process for polylactic acid production using Monascus, US Patent Aplication 2013/0224813, Assigned to Total Research & Technology Feluy S. A., August 29, 2013.
- 40. Mehta, R., Kumar, V., Bhunia, H., Upadhyay, S. N. *Journal of Macromolecular Science, Part C: Polymer Reviews* 45:325, 2005.
- 41. Rhim, J. W. Food Research International 51:714, 2013.
- 42. Cabedo, L., Feijoo, J. L., Villanueva, M. P., Lagarón, J. M., Giménez, E. *Macromolecular Symposia* 233:191, 2006.
- 43. Martin, O., Schwach, E., Avérous, L., Couturier, Y. Starch/Stärke 53:372, 2001.
- Chang, J. H., Uk-An, Y., Sur, G. S. Journal of Polymer Science, Part B: Polymer Physics 41:94, 2003.
- 45. Sinha Ray, S., Yamada, K., Okamoto, M., Ogami, A., Ueda, K. *Chemistry of Materials* 15:1456, 2003.
- Abeysekara, S. American Journal of Physiology-Endocrinology and Metabolism 293:558–565, 2007.
- 47. Naceur, B. M., and Gandini, A., eds. *Monomers, Polymers and Composites from Renewable Resources.* Elsevier, 2011.
- 48. James, L. Polymer Degradation and Stability 59 (1): 145–152, 1998.
- 49. Rudeekit, Y., et al. Journal of Metals, Materials and Minerals 18 (2): 83–87, 2008.
- Meredian, Inc. Polyhydroxyalkanoates. http://www.foodproductiondaily. com/Markets/Full-PHA-capacity-by-Q2-2014-says-Meredian, 2013.
- Snell, K. D., and Peoples, O. P. Biofuels, Bioproducts and Biorefining 3 (4) 456-467, 2009.
- 52. Saharan, B. S., Ankita, Sharma, D. *International Journal of Microbial Resource Technology* 1:11, 2012.
- 53. Kumar, P., Patel, S. K. S., Lee, J. K., Kalia, V. C. *Biotechnology Advances* 3:1543, 2013.
- Katırcıoğlu, H., Aslim, B., Yüksekdað, Z. N., Mercan, N., Beyatli, Y. African Journal of Biotechnology 2:147, 2003.
- Singh, G., Mittal, A., Kumari, A., Goel, V., Aggarwal, N. K., Yadav, A. European Journal of Biological Sciences 3:112, 2011.

- 56. Thirumala, M., Reddy, S. V., Mahmood, S. K. *Journal of Industrial Microbiology and Biotechnology* 37:271, 2010.
- Full, T. D., Jung, D. O., Madigan, M. T. Letters in Applied Microbiology 43:377, 2006.
- 58. Rhu, D. H., Lee, W. H., Kim, J. Y., Choi, E. Water Science and Technology 48:221, 2003.
- 59. Albuquerque, M. G. E., Torres, C. A. V., Reis, M. A. M. *Water Resources* 44:3419, 2010.
- 60. Moita, R., and Lemos, P. C. Journal of Biotechnology 157:578, 2012.
- 61. Reddy, C. S. K., Ghai, R., Rashmi, Kalia, V. C. *Bioresource Technology* 87:137, 2003.
- 62. Keshavarz, T., Roy, I. Current Opinion in Microbiology 13 (3): 321-326, 2010.
- 63. Misra, S. K., Valappil, S. P., Roy, I., Boccaccini, A. R. *Biomacromolecules* 7 (8): 2249–2258, 2006.
- 64. Misra, S. K., Valappil, S. P., Roy, I., Boccaccini, A. R. *Biomacromolecules* 8 (7): 2112–2119, 2007.
- Rehm, B. H. A., and Steinbüchel, A. *Journal of Biological Chemistry* 273 (37): 24044–24051, 2009.
- 66. Sudesh, K., Abe, H., Doi, Y. Progress in Polymer Science 25 (10): 1503–1555, 2000.
- 67. Valappil, S. P., et al. Antonie van Leeuwenhoek, 91 (1): 1-17, 2007.
- 68. Alastair, I., and Martin, A. N. Journal of Cleaner Production 45:38-49, 2013.
- 69. Nonato, R., Mantelatto, P., Rossell, C. *Applied Microbiology and Biotechnology* 57:1–5, 2001.
- Dammer, L., *et al.* Market developments of and opportunities for biobased products and chemicals, Report written for Agentschap NL, reference 52202, 2013.
- 71. Karina, P., et al. Trends in Food Science & Technology 10 (2): 52-68, 2008.

# Modification Strategies of Proteins for Food Packaging Applications

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#### Abstract

Biopolymers found in nature are complex molecules that adopt precise and definite shapes and structures. They comprise a diverse and versatile type of materials that normally exhibit useful properties such as biocompatibility, biodegradability, nontoxicity, adsorption capacity, film-forming ability and hydrophilicity. In addition, they can be tailored to confer important properties to meet specific needs and be modified to be useful in various applications such as food packaging. In general, biopolymers such as polysaccharides and proteins are widely used for this last application, in which the main objective is to maintain the quality and safety of the food products contained in the packaging for a specific time period. However, certain biopolymers do not show optimum properties to suit the use in food packaging due to their hydrophilic nature, poor mechanical properties and low thermal resistance. For these reasons, both modification and preparation strategies of these natural materials are commonly developed in order to obtain films with optimized properties for food packaging. This chapter focuses on synthetic strategies that can be used to improve specific properties of materials made from proteins, specifically from soy proteins. These improvements seek to satisfy the needs of the applications in which these materials will be used. General strategies such as the formation of chemical crosslinked networks using biodegradable and noncytotoxic agents; graft with synthetic monomers; physical mixture with nano-reinforcements and formation of a bilayer film using other components are described among others.

The extent and variety of the improvements made in the final properties of the films described using various modifications and preparation methodology open a

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promising field for the application of these "environmentally friendly materials," not only as coating or packaging materials, but also in varied and diverse applications in small and large scale.

*Keywords:* Biodegradable packaging, food packaging, protein-based materials for packaging, modification strategies of proteins, soy protein, soy protein as a base material for packaging, environmentally friendly materials, biopolymers

## 5.1 Biopolymers as Packaging Materials

The importance of packaging in the food supply chain is fully recognized [1]. It is known that the goal of food packaging is to maintain food safety and to minimize environmental impact. Furthermore, there must be a balance between the major role of packaging materials and their after-use issues [2]. One of the major concerns for the industry is food safety and quality. For this, several years ago, scientists studied various ways that try to extend the life of food and retain its nutritional properties and sensory characteristics. This adds to the peace of mind of consumers, since food is kept in good condition for longer.

The choice of the right materials for food packaging is critical since it must contain and protect food from damage and microbiological changes in their sensory attributes.

Synthetic polymers, specifically plastics, are the main packaging materials in high demand since they offer versatile solutions for several needs. They exhibit many advantageous characteristics such as transparency, softness, heat sealability, and good strength to weight ratio. In addition, they are generally inexpensive, show efficient mechanical properties such as tear and tensile strength, and are good barriers to oxygen and heat [3]. In spite of this, conventional packaging polymers have begun to be questioned due to increasing environmental concerns.

Nowadays, a great number of research studies focus on solving the problems produced by plastic waste in order to obtain environmentally friendly materials. For this reason, several researchers have studied the possibility of substituting the traditional petroleum-based plastics with biodegradable and low-cost materials with similar properties [4–7].

Therefore, the use of natural polymers or biopolymers as packaging materials may relieve the environmental impact caused by excessive use of conventional polymeric materials and thus reduce the increased production of plastics [8,9]. At present, the biopolymer concept is emerging. Biodegradable materials are associated with the use of renewable raw materials such as proteins and polysaccharides extracted from agricultural, plant and animal coproducts and byproducts, marine or microbial sources. These materials can be degraded by the environment (exposed to soil optimum moisture, microorganisms and oxygen) into simple substances (water and carbon dioxide) and biomass.

Similar to conventional packaging, biobased materials must fulfill a number of important conditions, including containment and protection of food quality, by serving as selective barriers to moisture transfer, oxygen uptake, lipid oxidation and losses of volatile aromas and flavors, maintaining food's sensory quality and safety [10–12].

The interest in biodegradable packaging has risen for several reasons. The materials from natural polymers are associated with poor properties and often they have inferior properties compared to commodity polymers. As opposed to most synthetic plastics used as packaging materials, most of the currently available bioplastics do not fulfill the key requirements of food packaging, especially in terms of barrier and mechanical properties [13].

Performing a modification technique is a way to improve properties and achieve property combinations required for specific applications. The chemical structure of biopolymers opens up possibilities for their reactive modification. The modification strategies of the starting material should be those that enhance the water resistance, the barrier effect against the flow of gases and the mechanical properties to avoid losses by rupture or break of the material, in order to achieve the incorporation of active ingredients to promote adhesion to the surface of food and to increase the stability to storage conditions. So, copolymerization, grafting, transesterification and the use of reactive coupling agents have been utilized with success to yield polymers with improved properties. Blending is another technique that allows considerable improvement in the impact resistance of brittle polymers.

However, further study is needed on the miscibility-structure-property relationships of these materials to utilize all potential of the approach. Several examples are shown for the various approaches and their outcome. Biopolymers and their blends are applied successfully in several areas from agriculture to consumer goods, packaging and automotive [13].

Biodegradable materials in the form of films may be used directly on the food or form one of the layers of the pack. In the first case, edible coatings are used (available on food surfaces by immersion or using the application of the filmogenic solution prepared by spray) or edible wrappings (or packaging) (in the form of a preformed layer by molding, thicker with respect to the edible coating), which are applied to the feed or used as a separator for different components of a food. Edible coatings form a semipermeable barrier to gases and water vapor, help to retain volatile components and may act as vehicles for food additives for developing active packaging (antimicrobials, antioxidants and flavoring). On the other hand, if the material forms part of a multilayer container, improvements in barrier properties against oxygen can be achieved and prevention of migration of compounds such as water, carbon dioxide, etc., can be reached.

In general, edible films often complement the nutritional value of the food, are healthy, minimally processed and do not contain chemicals agents; they prevent moisture loss during storage of fresh and frozen products, help keep the weight at the time of sale and decrease the rate of rancidity and discoloration. These are products that serve as packaging and are also used for the preservation of food, but they must meet conditions such as being free of toxic substances and having good sensory qualities.

The properties of the final materials useful for coating food are strongly influenced by the type of material used as matrix (conformation, molecular mass, charge), conditions of formation of the films (pH, temperature, concentration of components, solvent, etc.) and the type and concentration of additives. The development and the use of each biodegradable material depends on the characteristics of the substance concerned.

Undoubtedly, biopolymers mainly used in the preparation of biofilms are the polysaccharides, mainly starch, alginates and chitosan. Among renewable resources, starch is one of the most important polysaccharides obtained from plants. A biodegradable thermoplastic film can be tailored from starch with additives such as plasticizers to improve the processability by conventional plastic-forming equipments. Some authors have already been published on this subject and different plasticizers have been considered. The more usually used plasticizers include water, glycerol or sorbitol [14–16].

Alginates are the main biomacromolecules extracted from brown seaweed. In molecular terms, they are anionic linear copolymers of (1, 4) D-mannuronic acid and L-guloronic acid residues arranged in a nonregular blockwise pattern. They are nontoxic, biodegradable and biocompatible. The most interesting property of alginates is their ability to react with polyvalent metal cations, specifically calcium ions. The crosslinking with polyvalent cations can improve film properties like water resistance, mechanical resistance and barrier properties [8,17].

Chitosan is a weak cationic polysaccharide, formed mainly by (1, 4) 2-amino-2-deoxy-ß-D-glucan. It is a natural carbohydrate polymer derived from deacetylation of chitin, which is a major component of the shells of crustaceans such as crab, shrimp and crawfish. Because of its good film-forming property, biocompatibility and a certain degree of antimicrobial

activity, chitosan has often been chosen as a raw material to prepare composite films. Chitosan-based films have been proven to have adequate gas barrier properties, moderate mechanical properties, but high water vapor permeability (WVP) and water solubility because of their hydrophilic nature. To overcome these disadvantages, many researchers have investigated the polyelectrolyte complex (PEC) of chitosan with other polymers like sodium alginate, pectin, carrageenan and xanthan gum. These oppositely charged polysaccharides will form PECs that have interesting characteristics for controlled release applications [8,18–21].

## 5.2 Protein-Based Materials for Packaging

In their native state, proteins generally exist either as fibrous proteins, which are insoluble in water whose function in animal tissue is structural, or as globular proteins that are soluble in water or acidic, basic or saline aqueous solutions whose functions are various in living systems. Fibrous proteins are fully extended and associated closely together in parallel structures, generally through hydrogen bonding bridge to form fibers, while the globular proteins fold into complex spherical structures held together by a combination of hydrogen bridge bonds, ionic hydrophobic and covalent (disulfide). The chemical and physical properties of these proteins are dependent on chemical and structural composition.

Specifically, bioplastics and biofilms from protein feedstock may have significant advantages over traditional plastics, especially in areas such as packaging, agriculture, horticulture and medical materials.

Proteins are incredibly versatile materials, both by source and possibility for modifications to fulfill the diverse requirements of a specific application. Proteins can be a viable source of macromolecules for fiber, molded plastics, films, and an array of products currently supplied by the synthetic polymer industries. The significant advantages are based in the fact that some modified proteins can be processed using thermomechanical molding (e.g., compounding, extrusion, injection, compression) in a similar way as conventional petro-based polymers, are biodegradable, and available at relatively low cost. Besides, among the wide variety of biomaterials as storage materials, proteins generally occupy an important position, especially because they are usually extracted from subproducts of the food industry, as in the case of whey protein. For their ability to provide good oxygen barrier, such biopolymers are widely used as edible coatings because of their property of biodegradability. Also, sometimes they are combined with lipids such as beeswax and carnauba wax which provide resistance to steam for their hydrophobic properties, giving final composite materials with multiple properties. Other times, these proteins are combined with both lipids and polysaccharides in a single formulation, taking advantage of their own properties of each component and the synergy that occurs between them. Other active ingredients such as plasticizers, emulsifiers, surfactants, antimicrobial agents or antioxidants may be incorporated during processing into the films that act as supports, to help improve the mechanical properties, quality, flavor, nutritive value and conservation of food.

A number of researchers have developed bioplastics and biocomposites from plant-based proteins and addressed several challenges such as both the water and thermal stability of these materials [2–6].

A large number of proteins of different origin have been studied for their ability to form edible and/or biodegradable films [22–26]. The proteins of animal origin most studied [27–33] are caseins, whey proteins of milk [8], chicken egg white [7], collagen, gelatin, feather keratin [9,10], fish myofibrillar [11], and meat-and-bone meal [12]. These have also been used to develop bioplastics. It is common that these films from proteins demonstrate low toughness and water stability. These challenges and barriers need to be resolved [16]. On the other hand, proteins from vegetable sources, including those from wheat gluten, zeins from corn and sunflower [34– 45], have been widely studied. Particularly, protein from soybean has been extensively explored as an alternative to petroleum polymeric derivates in the manufacture of adhesives, plastics, and various binders [3]. Due to the importance of the use of soy protein isolate (SPI), specific modification strategies are described in Section 5.3 of this chapter.

As specific examples of uses, keratin (extracted from poultry feathers) and gelatin (collagen derived from connective tissue, among others) are used as raw material in the manufacture of edible films for meat products (sausages, meats, etc.) or fish. Protective covers for brownies and donuts were developed from sodium caseinate, cottonseed oil, soybean or corn and a plasticizer. Films from whey proteins are excellent barriers to oxygen but their mechanical properties are usually improved by the addition of glycerol. Heat is applied on the protein concentrate to denaturalize it and after cooling, the trapped gas is removed and the packaging material is formed. Thus, coatings are used in oxygen-sensitive products such as peanuts and walnuts to prevent oxidation.

In general, the modification of edible protein films to improve mechanical strength and moisture barrier properties can be realized by chemical methods, by enzymatic treatment, by combination with hydrophobic materials or by irradiation [46,47]. Various examples of modification processes of proteins in order to obtain edible and/or biodegradable films for food packaging are described in this chapter. In the same way, some examples of antimicrobial or other active film formulations are presented below.

Regarding formulations, the antimicrobial properties of various essential oils (clove, fennel, cypress, lavender, thyme and rosemary) were evaluated and were also tested in a fish-based extract, where clove and thyme were the most effective. Subsequently, gelatin-chitosan-based edible films containing clove essential oil were developed, and their antimicrobial activity was tested against six selected microorganisms: Pseudomonas fluorescens, Shewanella putrefaciens, Photobacterium phosphoreum, Listeria innocua, Escherichia coli and Lactobacillus acidophilus. The films containing clove inhibited all microorganisms independently of the film matrix or the type of microorganism. In a further experiment, the effect of the films with clove essential oil incorporated was analyzed during refrigerated fish storage, and microorganism growth was drastically reduced in the gram-negative bacteria, particularly enterobacteria, while the lactic acid bacteria remained practically constant during most of the storage period. The effect on microorganisms during this period was consistent with biochemical indices, indicating the viability of these films for the conservation of fish [48].

In another case of formulation, edible films based on chitosan, carboxymethyl cellulose and casein were formulated with several oleoresins (olive, rosemary, onion, pepper, cranberry, garlic and oregano) to inhibit or delay the effect of the microflora in squash pieces and to evaluate the effect on Listeria monocytogenes. The original film-forming solutions, without additives, showed no significant antimicrobial properties. The olive and rosemary oleoresins showed significant antimicrobial activity against both (native microflora in squash and L. monocytogenes). In general, solutions of films containing 1% of oleoresin showed different limited antimicrobial effects against these microorganisms. The native microflora was sensitive to chitosan with olive oleoresin, rosemary and pepper and carboxymethyl cellulose with rosemary. Furthermore, Listeria monocytogenes resulted sensitive to carboxymethyl cellulose with rosemary and very sensitive to film-forming solutions of chitosan with rosemary. Films of chitosan with olive and rosemary showed antioxidant properties by retarding the action of peroxidase (POD) and polyphenol oxidase (PPO) for five days of storage, but did not present deleterious effects on sensory acceptability of squash juice. Thus, the antioxidant protection of squash provided improved advantages in preventing browning reactions typically resulting in the loss of quality of fruits and vegetables [49].

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In the case of crosslinking reactions to modify proteins to form films, some examples are described as follows: the enzyme transglutaminase was used to produce cross linkages in the formation of edible films of casein, gelatin and casein-gelatin blends (100:0, 75:25, 50:50, 25:75 and 0:100). The introduction of the crosslinks induced formation of high molecular weight polymers, which resulted in changes in the mechanical and WVP properties of the films. The elongation of the final films containing different proportions of casein and gelatin, increased significantly compared to films obtained from gelatin or casein alone, providing a synergistic effect on the film properties; the greatest effect was observed for the formulation of casein-gelatin corresponding to the 75:25 ratio, showing elongation values of 27.2 and 56.8%, respectively, for samples with and without modification. This particular mixture showed a large decrease in WVP [50].

In another case, casein films were prepared by crosslinking with zein hydrolysate using transglutaminase. Wax was either incorporated into the film-forming solution or coated onto the casein films, improving their mechanical properties. The wax-incorporated films exhibited a greater reduction in tensile strength and Young's modulus than the wax-coated films. Besides, these exhibited a better improvement in flexibility of films than wax-coated casein films due to the plasticization effects of the incorporation of wax. On the other hand, the application of wax to casein films significantly improved their moisture barrier properties. The effectiveness of wax application on moisture barrier properties was greater in waxcoated casein films than wax-incorporated casein films. Therefore, coating wax emulsion on to the casein films was more effective than incorporating it into the films to improve moisture barrier properties of hydrophilic casein films [51].

Moreover, modifications on whey protein to yield edible films are described in several papers [52,53]. Cast films with different ratios of hydrolyzed and not hydrolyzed whey protein isolate (WPI) were produced. The influence of hydrolyzed WPI in whey protein isolate-based cast films on their techno-functional properties was investigated. This study showed that increasing hydrolyzed WPI concentrations significantly changes the mechanical properties while maintaining the oxygen and WVP. The tensile and elastic film properties decrease significantly by reducing the average molecular weight, whereas the yellowish coloration and the surface tension considerably increase. The strong intermolecular interactions of protein crosslinked by both disulphide and hydrogen bonding and by hydrophobic and electrostatic interactions into pure WPI-based cast films were reduced by the addition of glycerol as plasticizer. So, the mobility of polymer chains and thus film flexibility was achieved. The addition of glycerol also increases the free volume in the film leading to higher oxygen and WVP. This study showed the necessity to tailor the characteristics of whey protein isolate-based films according to their intended application and further processing [54].

In another case of modification, a doubly emulsified film incorporated with protein-polysaccharide microcapsules, which serves as a multifunctional food packaging film, thus as their properties, was investigated. Whey protein was selected by the emulsification and nutrition values and its general application in the field of edible films, while the polysaccharides were chosen according to their surface charges and emulsification ability. The relationships between the microstructural properties and controlled release features of a series of water-in-oil-in-water (W/O/W) microcapsulated edible films prepared in thermodynamically incompatible conditions were analyzed. The water-soluble riboflavin (VB2) nanodroplets dispersed in the liposoluble  $\alpha$ -tocopherol (vitamin E, VE) oil phase were embedded in whey protein-polysaccharide (WPs) microcapsules. These microcapsules were then integrated in WP films. Various polysaccharides, including gum arabic, low-methoxyl pectin, and k-carrageenan, exhibited different in vitro synergistic effects on the ability of both films to effect enteric controlled release of both vitamins [55].

Moreover, the combination of biopolymer films with barrier materials derived from petroleum-based plastics or aluminium to enhance their low barrier properties is an important subject. Because of this, research efforts are focused on the development of sustainable coatings, while maintaining the functional properties of the resulting packaging materials. An interesting article provides important information about the use of whey-based coatings for their barriers properties, and describes the properties of an innovative packaging multilayer material that includes a whey-based layer. The latter is able to serve as a good oxygen barrier and can either be used as an upper layer or as a sandwich layer in a composite. The whey protein formulations described resulted in excellent barrier properties almost comparable to the ethylene vinyl alcohol (EVOH) copolymers barrier layer conventionally used in food packaging composites. Various properties of the barrier layer such as good adhesion to the substrate and sufficient flexibility to withstand mechanical load while preventing delamination and/ or brittle fracture, are required. Whey-protein-based coatings have successfully met these functional and mechanical requirements. This study confirmed, in the case of multilayer configuration, that those coatings could be biodegraded using enzymatic detergent. This makes multilayer films recyclable, which is another good characteristic. On the other hand,

the multilayer packaging incorporating a whey-based barrier layer can be composted when using biodegradable polymeric substrates. Whey proteins are thus a promising resource for the packaging industry in that they provide a sustainable, recyclable packaging material that meets all the performance requirements of packaging materials [56].

In recent years, there has been a significant development in the production of vegetal proteins from a wide variety of vegetal sources and a tendency to reduce the consumption of animal protein because of vegetarian consumers. These plant sources are vegetables, cereals, oilseeds, root vegetables, greens, fruits, etc. They offer many characteristics and important properties. In general, the use of vegetal proteins has increased as they have no taste, their production is sustainable, they have less impact on the environment compared to animal proteins, are less expensive compared to those from animal sources, and allow the use of more innovative products.

## 5.3 SPI as a Base Material for Packaging

In particular, soy protein isolate (SPI) as raw material has shown advantages over other sources due to its exceptional film-forming properties, low cost (for its extensive production in several countries and for being isolated from oil industry waste) and good barrier properties to oxygen, aromas and lipids under low to intermediate moisture conditions [57]. This type of protein also produces softer, more transparent and flexible films compared to those derived from other sources [58]. However, SPI contains 58% polar amino acids that cause hydrophilicity [59], leading to brittleness in its wet state and poor moisture barrier and mechanical properties. These effects can be minimized using physical, chemical or enzymatic treatments including: blending with hydrophobic additives such as neutral lipids, fatty acids or waxes [60]; changing drying conditions [31]; enzymatic treatment with horseradish peroxidase [61]; heat curing [62]; UV irradiation [63]; and crosslinking. The  $\varepsilon$ -amino group of lysine is considered the primary reactive site between proteins and crosslinkers [64]. The crosslinkers most extensively used for proteins are aldehydic compounds such as glutaraldehyde [65-67], formaldehyde [67] glyoxal [68], epoxy [69] and phenolic compounds [70]. However, the cytotoxicity of these compounds restricts their use for food covering. For this, a new natural crosslinker, genipin (Gen), about 10000 times less cytotoxic than glutaraldehyde [71,72], is widely used. The colony-forming assay also showed that the proliferative capacity of cells after being exposed to Gen was approximately 5000 times greater than that of cells exposed to glutaraldehyde [71-73]. This

crosslinker is obtained from the enzymatic hydrolysis of *Genipa* with  $\beta$ -glucosidase [74]. *Genipa* is extracted from the fruit of a type of jasmine called *Gardenia Jasminoides Ellis*.

Flexible and homogeneous films could be obtained by casting method using glycerol as plasticizer and different amounts of Gen [44]. A dark blue color could be observed in the films that resulted from the chemical crosslinking of Gen with the amino groups on the SPI macromolecular chains. The color intensity and opacity linearly increased with the major amount of Gen added. After crosslinking reaction, the mechanical and physical properties of the resultant films were altered. Analyzing the physical properties, it could be noted that moisture content seems not to vary significantly. However, total soluble matter values showed a marked diminution depending on the amount of crosslinker incorporated. This resultant effect is particularly important since, when used as coating, such materials could be more resistant in the wet state. When the films were kept in contact with water, they showed softening and a subsequent swollen state. High crosslinking degrees allowed the formation of three-dimensional, rigid and less expansible structures with minor capacity for softening and swellability. A similar tendency was obtained for Gen crosslinked gelatin films [75]. The reduction in swelling ratio values reached in the crosslinked SPI films was the first evidence of SPI-Gen crosslinking reaction. Another effect derived from the crosslinking reaction of the films was the improvement in the mechanical properties. The tensile strength (TS) values increased until a limit value. Larger additions of Gen did not significantly vary the TS values. Furthermore, the elongation at break (E) values increased when Gen additions were minor or equal to a limit value. An increase in Gen concentration led to diminution in E values becoming a less deformable material. Also, WVP was measured, showing lower values which corresponded with smaller sizes of the pores in the films by the crosslinkings. A biodegradation test was developed to determine the biodegradation time of soilburied crosslinked films. As a result, the degradation of the different films strongly depended on the crosslinking degree, which was attributed to the hindering effect of the chemical networks on the enzymatic degradation [76]. The water absorption of the more crosslinked films resulted lower with respect to the less crosslinked. This effect produced diminution in the bioavailability of water inside the matrices and could explain the fact that microbial attack, proteolytic enzyme action and hydrolysis occurred to a lesser extent in the more crosslinked films, providing a longer biodegradation time.

Moreover, grafting reactions with different monomers were realized on SPI films to improve the properties. The formation of hybrid materials (containing natural and synthetic materials) represents another valid strategy [77] to enhance properties. A synergic effect can be produced between the advantageous properties of both materials; thereby the possibility of application is major. In particular, reactions of grafting of natural materials with different monomers is widely used [78]. These grafting reactions involve the incorporation of a pending synthetic polymer chain on the proteins chains.

So, grafting reactions using methyl methacrylate were performed on SPI using radical initiators, and then films were formed by heat compression method. The incorporation of poly(methyl methacrylate) in the material increased the hydrophobicity degree of the matrix producing macroscopic changes in its behavior against moisture. The films presented minor affinity to water, determined by the diminution in the moisture content, the total soluble matter and the water swelling demonstrated [79].

Another type of hybrid material can be formulated to yield nanoreinforced materials. Usually, nano-reinforcements which may be employed into different films are classified according to their dimensions in lamellar, fibrillar and particulates, although the latter are more studied, especially the nanocrystals formed from polysaccharides.

When nanocrystals produced from polar sources (such as polysaccharides) are used as nano-reinforcement in protein-based materials, the chemical structures of the matrix and filler are similar. The structural similarity promotes good miscibility and strong interfacial adhesion between the filler and the matrix. These interactions can be responsible for improving the basic properties of the final material. So, soy protein films nano-reinforced with starch nanocrystals (SNC) were developed by simple casting method [79]. The obtained films were transparent and homogeneous. The opacity and the degree of crystallinity increased with the amount of nanocrystals added. Moisture content, total soluble matter and swelling in water were evaluated, showing a marked effect of the SNC additions. As the amount of SNC increased, the films exhibited lower affinity for water due to the strong interactions occurring between the protein matrix and the reinforcement. A minor amount of moisture was present and the resultant products were less swellable in water. Moreover, mechanical properties were determined, showing that the films became more resistant (by increasing TS and Young's modulus) and less elongable (by decreasing E) as SNC aggregates increased. With a considerable amount of aggregates, an abrupt variation of these properties was noted [79].

Nevertheless, in some situations where the chemical or physical modifications do not accomplish good results or the improvements are not sufficient to fulfill the needs of a particular application, a blend polymeric system can be developed. In particular, the preparation of multilayer films employing two or more components is one of the alternatives of modification used, since the presence of each component can contribute their advantageous properties with an expected synergistic effect between them.

Soy protein-poly(lactic acid) bilayer films were prepared and studied for food packaging applications [76,80]. In particular, poly(lactic acid) (PLA) was selected because it is a biodegradable material whose use in food packaging is being currently developed. Some studies indicate that this material is equally suitable for such applications compared to the widely used low-density polyethylene [81]. In the two-component bilayer film, physical interactions exist between the components (hydrogen bond interactions between PLA carbonyl groups and hydrogen from peptide bonds of the protein). These interactions are responsible for the good stability and adhesion reached without using compatibilizing agents, adhesives, or without performing film surface chemical modifications.

The films were prepared using different proportions (%) of SPI/PLA and their physical and mechanical properties were studied. The analysis of the physical properties showed that the resultant films were more transparent when a high proportion of PLA was used. Furthermore, a major contact angle was determined for the PLA surface. Hence, it can be concluded that the resultant PLA layer was substantially more hydrophobic than SPI layer. The hydrophobicity of the PLA layer exhibited a different behavior against the action of water compared to the SPI film, conferring on the PLAcontaining films improvements in the properties. As expected, a marked decrease in the properties studied such as swelling, moisture content and total soluble matter were observed.

Furthermore, it is known that PLA has good barrier properties to water vapor [82]. Likewise, it was demonstrated after the permeability analysis was realized on the PLA-modified films, since values decreased. Thus, bilayer films reached lower WVP values compared to the SPI film. Other authors [83] described a multilayer system which exhibited a similar effect produced by PLA layers in protein films (gelatin). From the stress-strain curves, it was determined that the presence of PLA and the increase in its proportion produced diminution in E and a marked increase in TS and Young's modulus, which means that the material becomes less elongable and more resistant, turning into a more rigid material.

Biodegradation tests under soil burial conditions showed that after 55 days, the SPI film reached 100% of degradation while the 60/40 and 50/50 SPI-PLA films were degraded above 60 and 50%, respectively. These results suggest that the entire SPI layer was degraded while only a portion of PLA layer was degraded in the period analyzed. After 75 days, degradation

reached 80 and 65% for SPI-PLA 60/40 and 50/50, respectively. At this time, the PLA layer was partially degraded, showing a lowest degradation rate compared to the SPI component.

## 5.4 Conclusion

As described in this chapter, the development of biodegradable materials from natural sources focuses on the use of strategies to optimize fundamental properties so that all application requirements can be satisfied. A large part of the plastics used for every person includes packaging, especially food packaging. This is the reason why specific innovations are required in this field immediately. As can be noted in this text, the development of strategies that make proteins suitable for use as food packaging material is strongly increasing today. The current state of the environment can become more serious if no solutions to the replacement of traditional petroleum polymeric materials are found in a short period of time.

## References

- 1. Brody, A. L., Bugusu, B., Han, J. H., Sand, C. K., McHugh, T. H. Scientific status summary innovative food packaging solutions. *J Food Sci* 73:R107–R116, 2008.
- 2. Majeed, K. Potential materials for food packaging from nanoclay natural fibres filled hybrid composites. *Materials and Design* 46:391–410, 2013.
- 3. Robertson, G. State-of-the-art biobased food packaging materials. In *Environmentally Compatible Food Packaging*, ed. E. Chiellini. Woodhead Publishing, 3–28, 2008.
- 4. Jimenez, A., Fabra, M. J., Talens, P., Chiralt, A. Edible and biodegradable starch films: A review. *Food Bioprocess Technol* 5:2058–2076, 2012.
- Famá, L., Goyanes, S., Gerschenson, L. Influence of storage time at room temperature on the physicochemical properties of cassava starch films. *Carbohydrate Polymers* 70:265–273, 2007.
- Jiménez, A., Fabra, M. J., Talens, P., Chiralt, A. Effect of recrystallization on tensile, optical and water vapour barrier properties of corn starch films containing fatty acids. *Food Hydrocolloids* 26:302–310, 2012.
- Mali, S., Grossman, M. V. E., Garcia, M. A., Martino, M. N., Zaritzky, N. E. Effects of controlled storage on thermal, mechanical and barrier properties of plasticized films from different starch sources. *Journal of Food Engineering* 75:453–460, 2006.
- 8. da Silva, M. A., Iamanaka, B. T., Taniwaki, M. H., Kieckbusch, T. G. Evaluation of the antimicrobial potential of alginate and alginate/chitosan

films containing potassium sorbate and natamycin. *Packaging Technology and Science* 26:479–492, 2013.

- 9. Krochta, J. M., de Mulder Johnston, C. Edible and biodegradable polymer films: Challenges and opportunities. *Food Technology* 51:61–74, 1997.
- Roy, N., Saha, N., Kitano, T., Saha, P. Biodegradation of PVP-CMC hydrogel film: A useful food packaging material. *Carbohydrate Polymers* 89:346–353, 2012.
- 11. Sorrentino, A., Gorrasi, G., Vittoria, V. Potential perspectives of bionanocomposites for food packaging applications. *Trends in Food Science & Technology* 18:84–89, 2007.
- 12. Sharma, S., Luzinov, I. Water aided fabrication of whey and albumin plastics. *J Polym Environ* 20:681–689, 2012.
- Hendrix, K. M., Morra, M. J., Lee, H. B., Min, S. C. Defatted mustard seed meal-based biopolymer film development. *Food Hydrocolloids* 26:118–125, 2012.
- 14. Alix, S., Mahieu, A., Terrie, C., Soulestin, J., Gerault, E., Feuilloley, M. G. J., Gattin, R., Edon, V., Ait-Younes, T., Leblanc, N. Active pseudo-multilayered films from polycaprolactone and starch based matrix for food-packaging applications. *European Polymer Journal* 49:1234–1242, 2013.
- 15. Lourdin, D., Bizot, H., Colonna P. Antiplasticization in starch-glycerol films. *J Appl Polym Sci* 63:1047–1053, 1997.
- 16. Avérous, L., Boquillon, N. Biocomposites based on plasticized starch: Thermal and mechanical behaviours. *Carbohyd Polym* 56:111–122, 2004.
- 17. Alboofetileh, M., Rezaei, M., Hosseini, H., Abdollahi, M. Effect of nanoclay and cross-linking degree on the properties of alginate-based nanocomposite film. *Journal of Food Processing and Preservation* 38 (4):1622–1631, 2014.
- Yan, X. L., Khor, E., Lim, L. Y. Chitosan-alginate films prepared with chitosans of different molecular weights. *Journal of Biomedical Materials* 58:358–365, 2001.
- Bernabe, P., Peniche, C., Arguelles-Monal, W. Swelling behavior of chitosan/ pectin polyelectrolyte complex membranes: Effect of thermal cross-linking. *Polymer Bulletin* 55:367–375, 2005.
- 20. Naidu, V. G. M., Madhusudhana, K., Sashidhar, R. B. Polyelectrolyte complexes of gum kondagogu and chitosan as diclofenac carriers. *Carbohydrate Polymers* 76:464–471, 2009.
- Wang, Q., Dong, Z., Du, Y., Kennedy, J. Controlled release of ciprofloxacin hydrochloride from chitosan/polyethylene glycol blend. *Carbohyd Polym* 69:336–343, 2007.
- 22. Song, F., Tang, D. L., Wang, X. L., Wang, Y. Z. Biodegradable soy protein isolate-based materials: A review. *Biomacromolecules* 12 (10): 3369–3380, 2011.
- 23. Davis, G., Song, J. H. Biodegradable packaging based on raw materials from crops and their impact on waste management. *Industrial Crops & Products* 23:147–161, 2006.

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- 24. Tharanathan, R. Biodegradable films and composite coatings: Past, present and future. *Trends in Food Science & Technology* 14 (3):71–78, 2003.
- 25. Siracusa, V., Dalla, M. Biodegradable polymers for food packaging: A review. *Trends in Food Science & Technology* 19 (12):634–643, 2008.
- Kolybaba, M., Tabil, L. G., Panigrahi, S., Crerar, W. J., Powell, T., Wang, B. Biodegradable polymers: Past, present, and future. In ASAE Meeting Presentation 0300 (03):1–15, 2003.
- 27. Lacroix, M., Cooksey, K. *Edible films and coatings from animal origin proteins*, pp. 301–317, London: Academic Press, 2005.
- Deiber, J. A., Peirotti, M. B., Ottone, M. L. Rheological characterization of edible films made from collagen colloidal particle suspensions. *Food Hydrocolloids* 25 (5):1382–1392, 2011.
- Pei, Y., Yang, J., Liu, P., Xu, M., Zhang, X., Zhang, L. Fabrication, properties and bioapplications of cellulose/collagen hydrolysate composite films. *Carbohydrate Polymers* 92 (2):1752–1760, 2013.
- 30. Cao, N., Fu, Y., He, J. Preparation and physical properties of soy protein isolate and gelatin composite films. *Food Hydrocolloids* 21 (7): 1153–1162, 2007.
- Denavi, G. A., Pérez-Mateos, M., Añón, M. C., Montero, P., Mauri, A. N., Gómez-Guillén, M. C. Structural and functional properties of soy protein isolate and cod gelatin blend films. *Food Hydrocolloids* 23 (8):2094–2101, 2009.
- Harper, B. A., Barbut, S., Lim, L.-T., Marcone, M. F. Characterization of "wet" alginate and composite films containing gelatin, whey or soy protein. *Food Research International* 52 (2):452–459, 2013.
- Wang, L., Auty, M. A. E., Kerry, J. P. Physical assessment of composite biodegradable films manufactured using whey protein isolate, gelatin and sodium alginate. *Journal of Food Engineering* 96 (2):199–207, 2010.
- 34. Salgado, P. R., López-Caballero, M. E., Gómez-Guillén, M. C., Mauri, A. N., Montero, M. P. Sunflower protein films incorporated with clove essential oil have potential application for the preservation of fish patties. *Food Hydrocolloids* 33 (1):74–84, 2013.
- Salgado, P. R., Molina Ortiz S. E., Petruccelli, S., Mauri, A. N. Biodegradable sunflower protein films naturally activated with antioxidant compounds. *Food Hydrocolloids* 24 (5):525–533, 2010.
- 36. Arcan, I., Yemenicioğlu, A. Incorporating phenolic compounds opens a new perspective to use zein films as flexible bioactive packaging materials. *Food Research International* 44 (2):550–556, 2011.
- Beck, M. I., Tomka, I., Waysek, E. Physico-chemical characterization of zein as a film coating polymer: A direct comparison with ethyl cellulose. *International Journal of Pharmaceutics* 141 (1–2):137–150, 1996.
- Cho, S. Y., Lee, S. Y., Rhee, C. Edible oxygen barrier bilayer film pouches from corn zein and soy protein isolate for olive oil packaging. *LWT - Food Science and Technology* 43 (8):1234–1239, 2010.

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- 39. Ghanbarzadeh, B., Oromiehi, A. R. Biodegradable biocomposite films based on whey protein and zein: Barrier, mechanical properties and AFM analysis. *International Journal of Biological Macromolecules* 43 (2):209–215, 2008.
- 40. Irissin-Mangata, J., Bauduin, G., Boutevin, B., Gontard, N. New plasticizers for wheat gluten films. *European Polymer Journal* 37 (8):1533–1541, 2001.
- 41. Koehler, P., Kieffer, R., Wieser, H. Effect of hydrostatic pressure and temperature on the chemical and functional properties of wheat gluten III: Studies on gluten films. *Journal of Cereal Science* 51 (1):140–145, 2010.
- 42. Lens, J.-P., de Graaf, L. A., Stevels, W. M., Dietz, C. H. J. T., Verhelst, K. C. S., Vereijken, J. M., Kolster, P. Influence of processing and storage conditions on the mechanical and barrier properties of films cast from aqueous wheat gluten dispersions. *Industrial Crops and Products* 17 (2):119–130, 2003.
- 43. Roy, S., Gennadios, A., Weller, C. L., Testin, R. F. Water vapor transport parameters of a cast wheat gluten film. *Industrial Crops and Products* 11 (1):43–50, 2000.
- 44. González, A., Strumia, M. C., Alvarez Igarzabal, C. I. Cross-linked soy protein as material for biodegradable films: Synthesis, characterization and biodegradation. *Journal of Food Engineering* 106 (4):331–338, 2011.
- 45. Kim, K. M., Weller, C. L., Hanna, M. A., Gennadios, A. Heat curing of soy protein films at selected temperatures and pressures. *Water* 145:140–145, 2002.
- 46. Bourtoom, T. Edible protein films: Properties enhancement. *International Food Research Journal* 16:1–9, 2009.
- 47. Wittaya, T. Protein-based edible films: Characteristics and improvement of properties. In *Structure and Function of Food Engineering*, ed. A. A. Eissa. InTech, DOI: 10.5772/48167, 2012.
- Gómez-Estaca, J., López, de Lacey A., López-Caballero, M. E., Gómez-Guillén M. C., Montero, P. Biodegradable gelatin-chitosan films incorporated with essential oils as antimicrobial agents for fish preservation. *Food Microbiology* 27 (7):889–896, 2010.
- Ponce, A. G., Roura, S. I., del Valle, C. E., Moreira, M. R. Antimicrobial and antioxidant activities of edible coatings enriched with natural plant extracts: In vitro and in vivo studies. *Postharvest Biology and Technology* 49 (2):294– 300, 2008.
- 50. Grosso, C., Chambi, H. Edible films produced with gelatin and casein crosslinked with transglutaminase. *Food Research International* 39:458–466, 2006.
- 51. Sohail, S. S., Wang, B., Biswas, M. A. S., Oh, J.-H. Physical, morphological, and barrier properties of edible casein films with wax applications. *Journal of Food Science* 71:255–259, 2006.
- 52. Regalado, C., Pérez-Pérez, C., Lara-Cortés, E., García-Almendarez, B. Whey protein based edible food packaging films and coatings. *Advances in Agricultural and Food Biotechnology* 2006:237–261, 2006.
- 53. Jooyandeh, H. Whey proteins films and coatings: A review. *Pakistan Journal of Nutrition* 10:296–301, 2011.

#### 144 FUNCTIONAL POLYMERS IN FOOD SCIENCE

- Schmid, M., Hinz, L.-V., Wild, F., Noller, K. Effects of hydrolyzed whey proteins on the techno-functional characteristics of whey protein-based films. *Materials* 6:927–940, 2013.
- 55. Liu, F., Jiang, Y., Du, B., Chai, Z., Jiao, T., Zhang, C., Ren, F., Leng, X. Design and characterization of controlled-release edible packaging films prepared with synergistic whey-protein polysaccharide complexes. *J Agric Food Chem* 61:5824–5833, 2013.
- 56. Schmid, M., Dallmann, K., Bugnicourt, E., Cordoni, D., Wild, F., Lazzeri, A., Noller Schmid, K. M. Properties of whey-protein-coated films and laminates as novel recyclable food packaging materials with excellent barrier properties. *International Journal of Polymer Science* 2012:1–7, 2012.
- 57. Gennadios, A., Weller, C. L., Testin, R. F. Temperature effect on oxygen permeability of edible protein-based films. *Journal of Food Science* 58 (1): 212–214, 1993.
- 58. Guilbert, S., Gontard, N., Cuq, B. Technology and applications of edible protective films. *Packaging Technology and Science* 8 (6):339–346, 1995.
- Choi, S. G., Kim, K. M., Hanna, M. A., Weller, C. L., Kerr, W. L. Molecular dynamics of soy-protein isolate films plasticized by water and glycerol. *Journal* of *Food Science* 68:2516–2522, 2003.
- 60. Rhim, J. W. Increase in water vapor barrier properties of bioplymer-based edible films and coatings by compositing lipid materials. *Food Science Biotechnology* 13 (4):528–535, 2004.
- 61. Stuchell, Y. M., Krochta, J. M. Enzymatic treatments and thermal effects on edible soy protein films. *Journal of Food Science* 59 (6):1332–1337, 1994.
- 62. Gennadios, A., Ghorpade, V. M., Weller, C. L., Hanna, M. A. Heat curing of soy protein films. *American Society of Agricultural Engineers* 39:575–579, 1996.
- 63. Gennadios, A., Rhim, J. W., Handa, A., Weller, C. L., Hanna, M. A. Ultraviolet radiation affects physical and molecular properties of soy protein films. *Journal of Food Science* 63 (2):225–228, 1998.
- 64. Nayudamma, Y., Joseph, K. T., Bose, S. M. Studies on the interaction of collagen with dialdehyde starch. *Journal American Leather Chemist Asossiation* 56:548–567, 1961.
- 65. Park, S. K., Bae, D. H., Rhee, K. C. Soy protein biopolymers cross-linked with glutaraldehyde. *Journal of the American Oil Chemists' Society* 77 (8):879–884, 2000.
- 66. Bigi, A., Cojazzi, G., Panzavolta, S., Rubini, K., Roveri, N. Mechanical and thermal properties of gelatin films at different degrees of glutaraldehyde crosslinking. *Biomaterials* 22 (8):763–768, 2001.
- 67. Marquié, C. Chemical reactions in cottonseed protein cross-linking by formaldehyde, glutaraldehyde, and glyoxal for the formation of protein films with enhanced mechanical properties. *Journal of Agricultural and Food Chemistry* 49 (10):4676–4681, 2001.
- 68. Vaz, M. C. Processing and characterization of biodegradable soy plastics: Effect of cross-linking with glyoxal and thermal treatment. *J Appl Polym Sci* 97 (2):604–610, 2005.

- 69. Patil, S., Mark, R. D., Apostolov, J. E., Vassileva, A., Fakirov, E. Crystallization of water in some cross-linked gelatins. *Eur Polym J* 36 (5):1700–1706, 2000.
- Strauss, G., Gibson, S. M. Plant phenolics as cross-linker of gelatin gels and gelatin based coacervates for use as food ingredients. *Food Hydrocolloids* 18 (1):81–89, 2004.
- 71. Song, F., Zhang, L. Gelation modification of soy protein isolate by a naturally occurring cross-linking agent and its potential biomedical application. *Ind Eng Chem Res* 48:7077–7083, 2009.
- 72. Yuan, J. D., Chesnutt, Y., Utturkar, B. M., Haggard, G., Yang, W. O., Ong, Y., Bumgardner, J. L. The effect of cross-linking of chitosan microspheres with genipin on protein release. *Carbohyd Polym* 68 (3):561–567, 2007.
- 73. Sung, C. C., Huang, H. W., Huang, R. N., Tsai, L. L. H. In vitro evaluation of cytotoxicity of a naturally occurring cross-linking reagent for biological tissue fixation. *J Biomater Sci Polym Ed* 10 (1):63–68, 1999.
- 74. Fujikawa, J., Yokota, S., Koga, T., Kumada, K. The continuous hydrolysis of geniposide to genipin using immobilized β-glucosidase on calcium alginate gel. *Biotechnology Letters* 9 (10):697–702, 1987.
- 75. Bigi, A., Cojazzi, G., Panzavolta, S., Roveri, N., Rubini, K. Stabilization of gelatin films by crosslinking with genipin. *Biomaterials* 23:4827–4832, 2002.
- Martucci, J. F., Ruseckaite, R. A. Biodegradation of three-layer laminate films based on gelatin under indoor soil conditions. *Polymer Degradation and Stability* 94 (8):1307–1313, 2009.
- 77. Hou, A., Chen, H. Preparation and characterization of silk/silica hybrid biomaterials by sol-gel crosslinking process. *Materials Science and Engineering: B* 167 (2):124–128, 2010.
- 78. Kaur, I., Gautam, N. Synthesis and characterization of soy protein grafted polyethylene: Effect of reaction. *Malaysian Polymer Journal* 5 (1):39–54, 2010.
- 79. González, A. Materiales poliméricos biodegradables para ser usados en recubrimientos: Preparación por modificación de materiales de origen natural, Thesis Doctoral, 2013, Universidad Nacional de Cordoba, Cordoba, Argentina.
- González, A., Alvarez Igarzabal, C. I. Soy protein-poly (lactic acid) bilayer films as biodegradable material for active food packaging. *Food Hydrocolloids* 33 (2):289–296, 2013.
- 81. Koide, S., Shi, J. Microbial and quality evaluation of green peppers stored in biodegradable film packaging. *Food Control* 18:1121–1125, 2007.
- Siparsky, G. L., Voorhees, K. J., Dorgan, J. R., Schilling, K. Water transport in polylactic acid (PLA), PLA/polycaprolactone copolymers, and PLA/polyethylene glycol blends. *Journal of Environmental Polymer Degradation* 5:125– 136, 1997.
- 83. Martucci, J. F., Ruseckaite, R. A. Biodegradable three-layer film derived from bovine gelatin. *Journal of Food Engineering* 99 (3):377–383, 2010.

# **Films Based on Starches**

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#### Abstract

The film-forming ability of different native and modified starches by casting method is discussed in this chapter. Likewise, rheological properties of filmogenic suspensions are described. The mechanical and barrier properties of films, as well as microstructural characterization of these biomaterials are also discussed since they determine their performance and applications, mainly in food preservation. Characterization of films was carried out using different complementary techniques such as infrared spectroscopy (FTIR), light microscopy, scanning electron microscopy (SEM), atomic force microscopy (AFM), X-ray diffraction, differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA). Also, the plasticizer effect (glycerol and sorbitol) on films' properties was analyzed.

Even though film-forming capacity of different chemically modified corn starches was evaluated, this chapter only discusses the results concerning acetylated corn starch films. This selection was reliant on the lowest water vapor permeability of films based on this modified derivative.

Addition of specific additives to formulations modifies films functionality, transforming them into active films. Thus, in this chapter results concerning starch films with potassium sorbate are presented. Furthermore, antimicrobial agent diffusion from starch matrices is also discussed in order to demonstrate the effectiveness of these active films.

With the purpose to develop biodegradable packages, heat sealing capacity of native and acetylated corn starch-based films was studied. Film composition effect

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and presence of plasticizer on the type of heat sealing failure and its resistance is also discussed.

Thermoplastic starch (TPS) is a biodegradable material which can easily be adapted to different processes employing standard equipment used for synthetic polymers, such as extrusion, blowing, injection and compression molding. Thus, development of biodegradable films from TPS by extrusion and blowing methods is discussed. The relevance of this study lies essentially in the demonstration of the possibility to develop biodegradable films based on TPS employing industrial methods.

*Keywords:* Biodegradable starch films, acetylated starch, filmogenic suspension rheological behavior, mechanical and barrier properties, heat sealing capacity, film microstructure, active films, antimicrobial capacity, blown extrusion, thermoplastic starch

## 6.1 Introduction: General Aspects of Films Based on Native and Modified Starches

Interest in biodegradable and edible (B&E) films development from renewable resources is growing due to the increased environmental awareness and to a strong marketing trend towards more environmentally friendly materials. They can offer great potential to enhance food quality, safety and stability. Thus, a high interest has been shown in the production of materials from renewable resources, which are commonly known as bioplastics [1–6]. Biobased materials are promising as their feedstocks are renewable, theoretically they can be composted or recycled, and their production process may be more energy efficient than petroleum-based plastics processing [6]. They allow the control of mass transfer between components within a product, as well as between the product and the environment, and can offer improved product performance through the addition of additives such as antioxidants, antimicrobial agents and nutrients to their formulations. Biobased films development and their properties have been reviewed extensively in this book and previously [7–13].

Composition, microstructure and physical properties of biopolymeric films determine their possible applications. Controlling film formulation allows tailoring their mechanical and barrier properties, thereby improving their efficiency to preserve foods.

Among natural polymers, native starch is considered one of the most promising materials because an attractive combination of availability, price, performance and good film-forming ability, with regard to other biopolymers [10,14,15]. Thus, the functionality of starch edible films, in conjunction with their biodegradability compared with other polymers, could ensure their consideration in food packaging field in a near future.

Starch is a reserve polysaccharide present in the endosperm of cereal grains like corn (*Zea mays*), wheat (*Triticum aestivum o T. vulgare*) and rice (*Oryza sativa*); tubers like potato (*Solanum tuberosum*), cassava (*Manihot esculenta*), yam (*Dioscorea alata*), ahipa (*Pachyrhizus ahipa*); legumes like pea (*Pisum sativum*), okenia (*Okenia hypogaea*); and fruits like banana (*Musa paradisiaca*) and mango (*Manguifera indica*); among others [16]. According to their origin, starches present diverse physicochemical, structural and functional characteristics; they can be processed under different conditions and therefore they have many diverse end uses. Mainly, starch is employed in food industry to impart functional properties, modify food texture and consistency and so on. Current research is focused on using non-conventional starch sources since the actual starch portfolio does not cover industry's entire spectrum of requirements.

Starch owes much of its functionality to two major high-molecularweight carbohydrate components, amylose and amylopectin, as well as, the physical organization of these macromolecules within the granular structure [17]. Amylose, the linear polymer, is responsible for the filmforming capacity of starches. Besides, starches from different botanical sources present varied amylose/amylopectin ratio and several studies have demonstrated that these variations lead to obtaining biodegradable films with different mechanical properties [18–21].

Development and characterization of films based on native starches of diverse botanical sources have been widely studied by several authors [10,18,20,21–29]. Numerous studies can be found in the literature about corn starch films and their properties [10,15,20,26]. Development of B&E films is an interesting application for common and non-conventional starches since they could impulse their crops and grant added value to raw commodities.

Starch's hydrophilic nature is a major constraint that seriously limits starch-based materials applications since many of their properties depend on the ambient humidity [30]. An alternative to reduce these drawbacks is the use of modified starches [31]. Chemical derivatization has long been studied as a way to solve this problem and to produce low water-sensitive materials [32]. Chemical modification involves the introduction of functional groups into starch constituent molecules using reactions of derivatization (etherification, esterification, crosslinking and grafting) or reactions of decomposition (acid or enzymatic hydrolysis and oxidation). This is a useful alternative that allows modifying the structure and consequently the properties of native starches. Several authors have reported the

use of chemically modified starches to obtain films; mainly substituted and pregelatinized starches [32–35]. On the other hand, they were employed in the formulation of composite films by mixing with other biopolymers, such as gelatin [36] and  $\kappa$ -carrageenan [31], among others. In addition, modified starches, particularly starch esters, have been used in the preparation of biodegradable laminate films [37].

Besides, as for synthetic polymers, composition, microstructure and functional properties of films based on biopolymers determine their possible applications. Films formulation control allows tailoring mechanical and barrier properties of these materials, improving their efficiency to package food products.

Study of films' microstructure and the interactions between the components provides insight into both the fundamental aspects of material science and the practical technologies for future applications. Most of the methods used in the characterization of these materials are based on the study of structural and thermodynamic properties related to their crystalline-amorphous structure. X-ray diffraction is probably the most important technique for studying structural properties of crystalline solid materials, polymers and undoubtedly food materials [38,39]. Thermodynamic changes can be evaluated by several calorimetric techniques and by dynamic thermomechanical analysis [10,18,40–43]. Knowledge of molecular mobility and phase transitions are important since they affect films barrier properties, which define their performance under different conditions of common use and abuse.

This chapter discusses the film-forming ability of various native and modified starches. Rheological properties of filmogenic suspensions and mechanical and barrier properties of the obtained biomaterials are also described. A deep insight into films' microstructure is presented. Additionally, the heat sealing capacity of native and acetylated corn starch films was evaluated in order to develop biodegradable packages. Diffusion of antimicrobial agents such as potassium sorbate from active starch film is also discussed. Finally, development of biodegradable films from thermoplastic starch (TPS) employing industrial methods such as extrusion and blowing is described.

## 6.2 Characterization of Biodegradable Films Obtained by Casting from Different Native Starches and Acetylated Corn Starch

Starch is abundant in nature, commercially available, inexpensive and is totally biodegradable under a wide variety of conditions. Thus, it can be used in the development of completely degradable products for specific market needs. Of all polysaccharides of agricultural origin, starch has been the first to reach industrial applications. For example, Novamont, an Italian company, commercializes EverCorn<sup>TM</sup>, a starch-based material available as films or bags. Similarly, Bioenvelope, a Japanese company, commercializes Bio-P<sup>TM</sup>, another starch-based film. Likewise, Mater-Bi<sup>TM</sup>, a biodegradable material based on 60% starch and 40% alcohols produced by Novamont, is mainly commercialized in Europe and America.

Table 6.1 summarizes the main characteristics of starches from different sources which are relevant in B&E films development.

Generally, plasticizers are added to film formulations to aid processing operations and to modify final product properties. In the case of starchbased films, plasticizer addition overcomes materials' brittleness and improves their flexibility and extensibility. They are low molecular mass organic compounds that must be compatible with the film-forming polymers. Besides, plasticizers presence reduces intermolecular forces and increases polymer chain mobility [44]. Oligosaccharides, polyols and lipids are different types of plasticizers chemically compatible with hydrocolloid-based films; glycerol being the most widely use [15,36,45–50].

Additional additives, including antioxidants, antimicrobial agents and nutrients, can be incorporated into film formulations in order to achieve

Starch source	Amylose content (%)	Granule size (μm)	X-ray crystalline pattern	Gelatinization temperature (°C)
Corn [21]	23.9	11.5	А	72.2
Cassava [21]	15.5	8.8	В	69.9
Ahipa [21]	11.6	9.4	С	67.2
Okenia [23]	26.1	1-3	С	71.2
Mango [23]	28.7	5-10	С	73.8
Banana [23]	35	10-40	С	77.6
Yam [43]	30	45.3	В	76.0

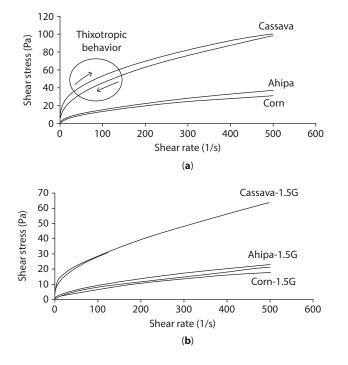
 Table 6.1 Main characteristics of starches from different sources.

specific functionalities. This concept of "active films" is very promising for the future, as it creates new avenues for designing packaging materials according to product needs.

### 6.2.1 Rheological Behavior of Filmogenic Suspensions

The first step to prepare filmogenic suspensions is the gelatinization of native starch granules, either by cold (e.g., alkaline treatment with NaOH) or thermal treatments, the latter being the most common technique. However, alkaline dispersion can be used to alter size distribution of starch constituent molecules since the conditions of this method favor a mild degree of starch hydrolysis or depolymerization [23,51]. Thus, material properties could be modified to fit the application needs. In general, plasticizers are added to gelatinized starch suspensions, as well as other functional additives (e.g. emulsifiers, lipids and antimicrobial or antioxidant agents). It must be stressed that each individual additive may require particular conditions for an appropriate and effective incorporation.

Rheological behavior of filmogenic starch suspensions determines their processing conditions to obtain films at industrial scale. Furthermore, rheological properties are related to the presence of some defects such as bubbles and pores in polymeric matrixes [52]. Rotational assays led to the analysis of rheological behavior of starch pastes when they are submitted under conditions close to industrial processing parameters such as high shear stress. Figure 6.1 shows flow curves corresponding to gelatinized starch suspensions from different sources, with and without glycerol as plasticizer. All filmogenic suspensions presented a pseudoplastic behavior (n < 1), which was satisfactorily adjusted by the Ostwald-de Waele model. Moreover, gelatinized starch suspensions were characterized as thixotropic ones, indicating that rheological behavior of these systems was time dependent (Figure 6.1a). Thixotropic materials exhibit decreasing shear stress and apparent viscosity over time at a fixed shear rate [53]. Rheological properties of starch pastes depend on their botanical sources and determine their most adequate use in food processing. Cassava starch filmogenic suspensions presented significantly (p < 0.05) higher apparent viscosity values, indicating that the remainder amylopectin inside starch granules reinforces the amylose network. Furthermore, macromolecules' structural characteristics (molecular weight, polymerization degree, chains size distribution, etc.) determine degree of network reinforcement. Figure 6.1b shows that glycerol addition to filmogenic suspensions did not modify their flow behavior, although the apparent viscosity at 500 s<sup>-1</sup> values



Native starch	Glycerol (% w/w)	r <sup>2</sup>	Flux behavior index (n)	Consistency index (k) (Pa/s <sup>n</sup> )	Apparent viscosity at 500 s <sup>-1</sup> (mPa s)
6	0	0.9985	0.60±0.01	11.78±1.77	220.4±36.4
Cassava	1.5	0.9990	0.51±0.02	1.26±0.08	126.3±6.2
Ahipa	0	0.9722	0.45±0.03	2.59±0.70	81.4±6.8
	1.5	0.9963	0.66±0.05	0.45±0.03	44.0±2.6
Corn	0	0.9982	0.51±0.01	1.24±0.09	60.0±2.4
Com	1.5	0.9950	0.64±0.04	0.42±0.01	34.9±1.2

**Figure 6.1** Flow curves and rheological parameters of ahipa, cassava and corn starch filmogenic suspensions: (a) without glycerol and (b) with 1.5% w/w glycerol (1.5 G). Arrows indicate the up and down flow curves.

decreased significantly (p < 0.05). Lipids can be added to the starch system in order to decrease the permeability of the films [54]. Table 6.2 shows that both plasticizer and lipid addition to corn starch gelatinized suspensions decreased the flow behavior index, and increased the consistency index. Apparent viscosity of corn starch suspensions decreased with the addition of both plasticizer and lipid (Table 6.2).

Oscillatory assays evaluate starch pastes viscoelastic behavior within linear viscoelasticity range where sample did not suffer structural damage. Figure 6.2 shows mechanical spectra obtained from frequency sweeps of corn, cassava and ahipa starch filmogenic suspensions. Corn starch

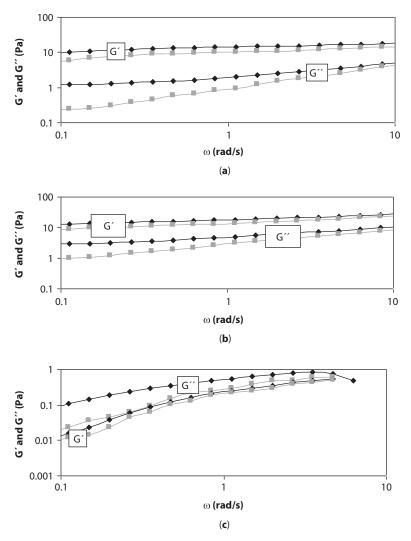
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Corn starch filmogenic suspension (20 g starch/ L)	Apparent viscosity $(\eta_{ap})$ at shear rate 692.48 s <sup>-1</sup> (mPa.sec)
Without additives	$12.85 \pm 0.063$
20 g/L Glycerol (G)	$11.95 \pm 0.182$
G + 2 g/L Sunflower oil (SO)	11.31 ± 0.092
20 g/L Sorbitol (S)	$12.59 \pm 0.176$
S + SO	9.64 ± 0.182

**Table 6.2** Formulation effect on apparent viscosity of corn starch filmogenicsuspensions.

filmogenic suspensions presented a typically viscous fluid behavior since higher viscous module values compared to elastic ones (G'' > G') were registered over almost all frequency ranges, approaching each other at high frequency values (Figure 6.2a). While, for ahipa and cassava starch pastes, G' values were significantly higher (p < 0.05) than G" ones, and remained practically constant throughout all the analyzed frequency ranges, behaving like a weak gel (Figure 6.2b and c). The G' and G" values for cassava starch gelatinized suspensions were higher than those of ahipa and corn starch pastes. For example, at 1.1 Hz, G' and G" of cassava starch pastes were 20 and 60% higher, respectively, than the corresponding values of ahipa starch pastes. These results are in agreement with the apparent viscosities reported previously (Figure 6.1). When glycerol was incorporated to starch matrixes, both G' and G" decreased; however the curves tendency was similar to those corresponding to unplasticized films (Figure 6.2). A similar trend was reported by Rodríguez-González et al. [55] for wheat thermoplastic starch films plasticized with different glycerol concentrations.

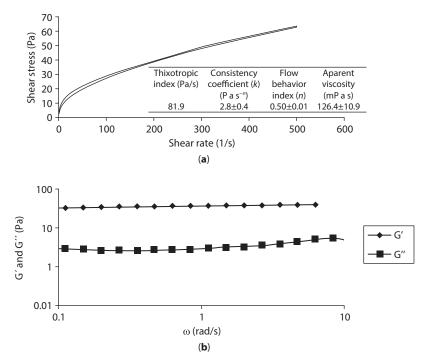
On the other hand, chemical modification of starch granules can affect the rheological behavior of filmogenic suspensions. Figure 6.3a shows the rheological flow curve corresponding to gelatinized acetylated starch suspension (5% w/w) with glycerol (1.5 g/100g starch), exhibiting a pseudoplastic behavior which could be fitted to the Ostwald-de Waele model. From stress sweep assays, it was determined that linear viscoelasticity range was extended up to 2.7 Pa, indicating that gelatinized suspensions based on the acetylated corn starch presents a high deformation resistance suitable to withstand severe processing conditions [15]. Figure 6.3b shows dynamical spectra obtained for acetylated corn starch gelatinized suspensions, presenting a typical behavior of a viscous fluid, since G'' resulted higher than G' values along all the assayed frequency range, behaving like a gel.



**Figure 6.2** Mechanical spectra, at constant amplitude (1 Pa) of 5% w/w starch filmogenic suspensions without (�) and with 1.5% w/w of glycerol (•): (a) ahipa; (b) cassava and (c) corn.

### 6.2.2 Film Properties

Casting is a common and small-scale production method used to obtain biodegradable films. In this technique, filmogenic suspension is poured onto acrylic plates, and then dried in a ventilated oven to a constant weight. This simple technique produces B&E films that can be easily removed from plates. Besides, in the casting method film thickness can be adjusted by



**Figure 6.3** Acetylated corn starch filmogenic suspensions with 1.5% w/w glycerol: (a) flow curves and rheological parameters and (b) viscoelastic behavior.

controlling the ratio of filmogenic suspension weight and the plate area. Drying conditions (rate and temperature) determine film characteristics (e.g. water content, crystallinity, etc.), affecting its microstructure and properties. Bader and Goritz [56] stressed that by tailoring drying conditions amorphous-crystalline structure could be controlled, which is strongly related to the barrier and mechanical properties of films.

At industrial scale, starch-based films can be obtained by the thermocompression, blowing or lamination process, similar to those used for synthetic ones.

The main attributes involved in biodegradable films characterization are: optical properties, water solubility, water sorption/desorption, microstructure, biopolymer compatibility (composite films), thermal behavior, barrier properties (vapor and gaseous permeability) and mechanical performance.

## 6.2.2.1 Optical Properties

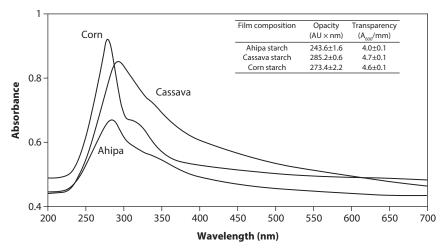
Films optical properties ultimately determine packaged product acceptability by consumers. Material opacity is a critical property to consider if the film is useful to develop packaging which allows seeing the packed product. It can be measured using the method proposed by Gontard *et al.* [38], in which the absorption spectrum is recorded over the visible range. Opacity is estimated as the area under the curve (Au x nm); transparent films are characterized by low values of this area. Table 6.3 shows that chitosan films were the most transparent and corn starch (CS) ones the most opaque, increasing opacity with starch concentration. Nevertheless, opacity values for starch-based films were still lower than those reported for wheat gluten films obtained under different solubilization conditions [38].

On the other hand, study of UV light absorption capacity of biodegradable films is relevant to determine their possible applications for food packaging. Materials which are able to absorb UV light could be useful to extend shelf life of fatty foods that are susceptible to oxidative rancidity. Otherwise, films that cannot absorb in this spectral region could be used to develop packages for foods which will be later sanitized by UV light exposure. Starch-based films spectra exhibited a characteristic peak at 270–300 nm, resulting in barriers to UV light (Figure 6.4). Ahipa starch led to the development of films with a lower capacity to absorb UV light since the peak intensity was lower compared with cassava and corn starches (Figure 6.4). Transparency values of cassava and corn starch films were similar to

Film formulation	Film opacity (Au x nm)	Film color		
		Color differences (Δ <i>E</i> )	Chromaticity parameter <i>b</i> *	
Corn starch <sup>a</sup> (CS)	$138.0\pm0.8^{\rm b}$	$0.83 \pm 0.16$	$2.20\pm0.25$	
CS with glycerol (2g/ 100g)	109.6 ± 0.9	$0.60 \pm 0.10$	$2.23 \pm 0.08$	
CS with chitosan (50:50)	95.9 ± 1.05	$1.74\pm0.15$	$2.94 \pm 0.15$	
CS with glycerol and chitosan	88.7 ± 0.7	2.16 ± 0.19	3.68 ± 0.21	
Chitosan (1g/100)	$18.9 \pm 1.1$	$3.79\pm0.50$	$5.04 \pm 0.32$	

 Table 6.3 Optical properties of corn starch, chitosan and composite films.

<sup>a</sup> CS concentration: 5g/100g filmogenic suspension, <sup>b</sup> value ± standard deviation



**Figure 6.4** UV–vis light absorption spectrum and optical properties of starch films (ahipa, cassava and corn) plasticized with 1.5% w/w of glycerol.

those corresponding to some synthetic films, such as polyvinyl dichloride (PVDC, 4.58 A600/mm).

## 6.2.2.2 Water Solubility

Water solubility of starch films is another relevant property which determines the application of these materials. In some cases, water-insoluble films are required to enhance product integrity and package humidity resistance. In applications such as additive encapsulation, total or partial film dissolution could be useful [26]. Films water solubility at 25 and 100°C are shown in Table 6.4. Starch type did not affect film water solubility, regardless of the assayed temperature. Values increased significantly (p < 0.05) with temperature and glycerol addition due to plasticizer hydrophilic characteristic. Similar results were reported by Shen *et al.* [57] and Piermaría *et al.* [58] for sweet potato starch films with glycerol and for plasticized kefiran films, respectively.

## 6.2.2.3 Water Sorption Isotherms

Water sorption isotherms are useful for the estimation of film stability under different ambient conditions. Particularly, in the case of film based on hydrocolloids, this study is relevant since these materials are very sensitive to relative humidity. Although sorption isotherms can be measured by several techniques, a simple procedure was described by Spiess and Wolf [59].

Film formulation (starch concentration 5/100g)	Water solubility (%)		
	at 25°C	at 100°C	
Ahipa	$3.8\pm0.4^{a}$	$17.2 \pm 0.7$	
Ahipa – 1.5G	$13.2 \pm 0.1$	26.6 ± 1.1	
Cassava	$3.9 \pm 0.0$	$17.0 \pm 0.6$	
Cassava – 1.5G	$13.6 \pm 0.3$	$27.7 \pm 1.3$	
Corn	$4.0 \pm 0.3$	$16.4 \pm 2.9$	
Corn – 1.5G	$13.6 \pm 0.0$	$26.3\pm0.5$	

**Table 6.4** Water solubility of ahipa, cassava and corn starch films without andwith 1.5% w/w glycerol (1.5G).

<sup>a</sup> value ± standard deviation

1.5G = 1.5g glycerol/100g

Sorption isotherms for yam starch films (with and without glycerol) and native yam starch were compared at 25°C (Figure 6.5). All isotherms showed a similar sigmoid shape (type II isotherm). When samples were conditioned at water activity ( $a_w$ ) values greater than 0.43, plasticized starch film showed higher equilibrium moisture contents than both native yam starch powder and non-plasticized starch film. Hygroscopic characteristics of glycerol-plasticized starch films could be attributed to the hydrophilic character of this plasticizer.

Control films showed higher equilibrium moisture content than the native yam starch at  $a_w > 0.75$ . This result could be attributed to the fact that during film production, gelatinization led to a starch molecule reorganization, increasing water absorption capacity of the unplasticized film compared to native starch. Unplasticized films showed similar behavior to those reported by other researchers working with high amylose corn starch films [56] and tapioca starch films [60].

With regard to acetylated starch-based films, experimental data can be satisfactorily fitted to the GAB model, estimating water content values of the monolayer ( $X_m$ ) (Figure 6.6). Plasticized films exhibited significantly higher  $X_m$  values (0.127 g water/g dry solid) than unplasticized ones (0.063 g water/g dry solid). Coupland *et al.* [61] reported a similar trend for whey protein films plasticized with different concentrations of glycerol. Müller *et al.* [62] reported a water content value of the monolayer of 0.094 g water/g dry matter, for cassava starch films plasticized with glycerol.

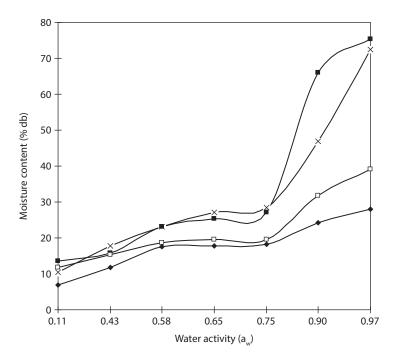
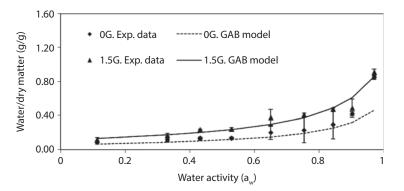


Figure 6.5 Water sorption isotherms of yam starch films.



**Figure 6.6** Water sorption isotherms of acetylated corn starch films without glycerol (0G) and with glycerol 1.5% w/w (1.5G).

#### 6.2.2.4 Microstructure

Biodegradable films' microstructure provides the physical basis for their barrier and mechanical properties. Common techniques used to elucidate film structure include scanning electron microscopy (SEM), atomic force microscopy (AFM), X-ray diffraction (XRD), differential scanning calorimetry (DSC), thermomechanical analysis (TMA), dynamic mechanical analysis (DMA) and Fourier transform infrared spectroscopy (FTIR).

### 6.2.2.4.1 Scanning Electron Microscopy (SEM)

Scanning electron microscopy may be used to evaluate film homogeneity, layer structure, pores and cracks, surface smoothness and thickness. Figure 6.7 shows SEM micrographs of cryofractured surfaces of plasticized films based on ahipa, cassava and corn starch. Materials based on corn starch exhibited a more homogeneous and compact structure than films obtained from tuberous starches. Compact and homogeneous matrix of films is an indicator of structural integrity and, consequently, good mechanical properties (high resistance and elongation at break) are expected.

Unplasticized acetylated starch films exhibited a multilayer structure (Figure 6.8a). Glycerol addition increased, on average 20%, film thickness, which could be related to a modification of the film structure (Figure 6.8b). It is well known that glycerol interferes in chain interactions [50], and thus the typical multilayer structure of unplasticized films was not observed.

## 6.2.2.4.2 Atomic Force Microscopy (AFM)

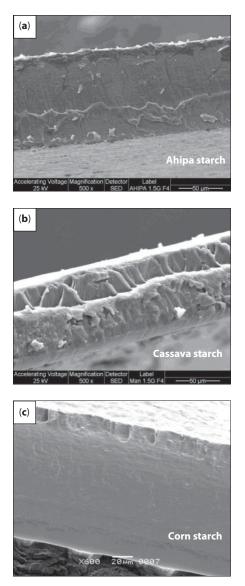
Topography and roughness of starch films surfaces can be evaluated using a multimode atomic force microscope. Images were obtained in tapping mode using a silicon nitride tip model NP20 (Veeco Instrument Inc., NY, USA). Images of films surfaces were randomly taken at different locations of the specimens to obtain reliable and reproducible data. The 2D and 3D images were analyzed with the Scanning Probe Microscopy WSxM 3.1 software. To evaluate film surface roughness the following statistical parameters were calculated: ironed surface (three-dimensional image area, correspond to the sum of the areas of all triangles formed by three adjacent points; nm<sup>2</sup>) and RMS (height standard deviation; nm). Figure 6.9 shows 3D topographic images of films based on native and acetylated corn starch films.

Use of acetylated starch in the formulations allowed the development of films whose surfaces were softer with lower roughness, evaluated by the standard deviation of the heights (RMS). It was also determined that the addition of plasticizer decreased roughness parameters of starch film surfaces (Figure 6.9).

### 6.2.2.4.3 Infrared Spectroscopy

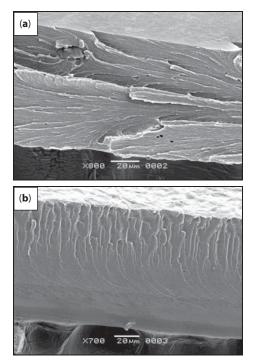
Fourier transform infrared spectroscopy (FTIR) is a useful technique to complement microstructural characterization of films and may be used to evaluate interactions between the corresponding components. The FTIR spectra of native corn starch films without glycerol showed typical signals

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**Figure 6.7** SEM micrographs of (a) ahipa, (b) cassava and (c) corn starch films plasticized with 1.5% w/w of glycerol.

of stretching, bending and deformation for the main characteristic functional groups of starch (Figure 6.10). Acetylated corn starch films presented the same signals that native starch ones and a characteristic peak located at 1726 cm<sup>-1</sup>, which is specific to CO bond stretching vibration of acetyl groups [63]. Furthermore, Guerra Della Valle *et al.* [64] observed a

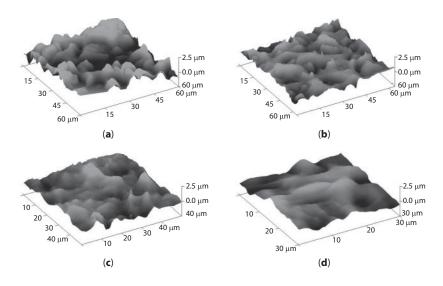


**Figure 6.8** SEM micrographs of acetylated corn starch based films: (a) without plasticizer and (b) with 1.5% w/w glycerol.

decrease in the vibration signal corresponding to stretch  $(3000-3900 \text{ cm}^{-1})$  and bending vibration  $(1650 \text{ cm}^{-1})$  of the OH groups due to the introduction of acetyl substituents on the starch constituent molecules.

## 6.2.2.4.4 X-ray Diffraction (XRD)

X-ray diffraction patterns show an amorphous-crystalline structure characterized by sharp peaks associated with crystalline diffraction and an amorphous zone; the higher the amorphous zone, the lower the crystallinity. Amorphous regions within the sample can be estimated by the area between the smooth curve drawn following the scattering hump and the baseline joining the background within the low- and high-angle points. Crystalline fraction can be estimated by the relative area of the upper regions above the smooth curve [65,66]. In general, film crystallinity is dependent on the following processing conditions: i) biopolymer source and plasticizer, ii) completeness of biopolymer dissolution in water, iii) film drying conditions (rate and temperature), and iv) final moisture content of the samples [67,68]. The shape and width of the diffraction profile are determined by both the mean crystal size (and distribution of crystal



Film formulation		Roughness parameters			
Corn starch	Glycerol (% w/w)	RMS (μm)	Mean roughness (μm)	lroned surface (μm²)	
Native	0	0.5407	0.4247	3954.93	
	1.5	0.506	0.3939	2627.71	
Acetylated	0	0.3625	0.2883	3744.49	
	1.5	0.3113	0.2431	2634.89	

**Figure 6.9** AFM topographic images (3D) of films based on: (a) native corn starch, (b) native corn starch with 1.5% w/w glycerol, (c) acetylated corn starch and (d) acetylated corn starch with 1.5% w/w glycerol. Effect of formulation on film roughness parameters.

size within the specimen) and the particular imperfections of the crystalline lattice [69].

X-ray diffraction can be used to track the recrystallization of film polymers during storage. In the case of starch-based films, peak width decreased slightly and peak intensities increased, indicating a growth in crystallite size corresponding to a slow recrystallization process. X-ray diffraction patterns of composite films generally represent a mixture of component features in which the characteristic peaks of the individual components can be identified.

Film preparation techniques may also lead to the development of different matrix structures. For films based on starch thermally gelatinized, X-ray diffraction pattern of yam starch exhibited a B-type crystalline packing arrangement, characteristic of starch from tubers [70]; this pattern

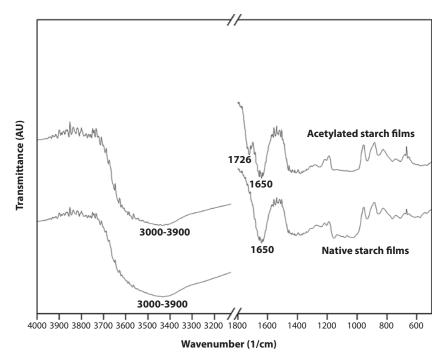
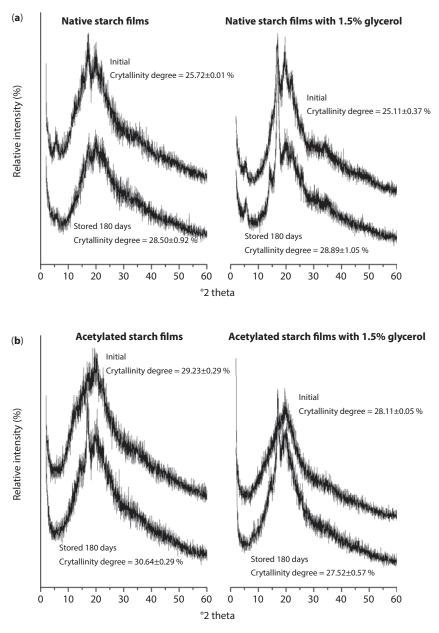


Figure 6.10 FTIR spectra of films based on native and acetylated corn starch.

remained virtually unchanged over the course of storage. Starch and glycerol contents did not markedly influence the X-ray pattern of these films [18]. In contrast, when films were obtained from starch solubilized by alkaline treatment, X-ray diffraction patterns showed a crystalline structure of higher stability, namely A-type pattern (Figure 6.11). This change in the crystalline pattern was also observed for amylomaize films by Bader and Goritz [56], and was also attributed to film drying conditions. For temperatures up to 60°C, diffractograms of films exhibited a B-type crystalline pattern, while those dried at 100°C exhibited diffractograms corresponding to A-type crystals. As film drying temperature increased over the range of 60 to 100°C, film diffractograms exhibited a continuous transition from B- to A-type crystals. A film's crystallinity was primarily related to the starch amylose content, and depended on both drying and storage conditions. Water is incorporated in a structural active state through inter- and intramolecular hydrogen bondings [71]. High water content favors chain interactions and, consequently, starch crystallization.

Starch films without plasticizer showed higher crystallinity than those containing plasticizer, showing a larger amorphous zone and lower peaks (Figure 6.11a). Films containing plasticizer also retained a stable diffraction



**Figure 6.11** X-ray diffractograms of films based on: (a) native and (b) acetylated corn starch. Initial and stored 180 days at 20°C and 63.8% RH.

pattern during the initial storage stages, while unplasticized starch films required more time to reach a stable diffraction pattern [51]. Nevertheless, the presence of glycerol facilitated polymeric chain mobility, allowing rapid development of the most stable structure, and also reduced crystal growth by interfering with polymeric chain arrangement.

Acetylated starch-developed films yielded less crystalline structure than those from native starch (Figure 6.11b).

## 6.2.2.4.5 Differential Scanning Calorimetry (DSC)

Evolution of film matrix crystalline structure during storage can also be evaluated by DSC, which allows the determination of glass transition temperature (Tg). As described for X-ray diffraction, film preparation and storage conditions influence their thermal transitions. Films obtained by starch thermal treatment, such as those formulated with yam starch, did not show any peaks in DSC thermograms at the beginning of the storage time, indicating that starch gelatinization during film production was complete. With storage (90 days at 20°C and 64% relative humidity), these films did not show any peaks in DSC thermograms (between 40 and 120°C), indicating the stability of the matrix [18]. A similar trend was observed for native starch films from other botanical sources, as well as those based on acetylated corn starch.

However, starch films obtained by alkaline treatment showed an endothermic transition at around 50°C during storage (90 days); this peak became narrower and its melting temperature and the corresponding enthalpy ( $\Delta$ H) increased with storage time (Figure 6.12). This thermal transition could be associated with several processes, such as crystal growth of short chains (products of hydrolysis), recrystallization of amylose or other long lateral amylopectin chains.

As previously described for XRD analysis, the presence of plasticizers limited starch crystal growth and recrystallization, leading to lower enthalpy values ( $\Delta$ H) and peak melting temperatures (Figure 6.12). Sorbitol is a good starch plasticizer since its molecular structure is similar to the glucose units of constituent molecules of starch, increasing the chances to interact with the polymeric chains [51]. Additives may interfere with the polymeric chains association due to steric hindrances, and in these cases the crystallinity of films will likely decrease.

## 6.2.2.4.6 Glass Transition Temperature (Tg)

Glass transition temperature  $(T_g)$  is strongly dependent on both film composition and moisture content, and it can be seen as a film stability parameter. As the water content of an amorphous material increases,  $T_g$ 

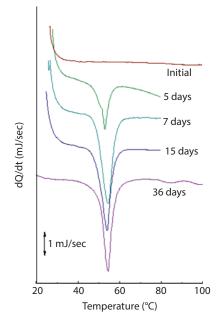


Figure 6.12 DSC of starch films obtained by alkaline treatment.

decreases. Thus, for a given storage temperature, an amorphous matrix in the glassy state remains stable to molecular change, while the same matrix at higher moisture content (corresponding to the rubbery state) can undergo molecular reorganization. In the rubbery state, polymer chains possess sufficient mobility for crystal growth and perfection. Thus, knowledge of T<sub>g</sub> is important since it impacts on films mechanical and barrier properties under specific application and storage conditions.

Both DSC and thermo-mechanical analysis (TMA) techniques are commonly used to estimate  $T_g$ . Chang and Randall [72] stressed that TMA sensitivity is superior to that of DSC for defining glass transition temperatures. Dynamic mechanical thermal analysis (DMTA) may also be used for  $T_g$  determination. Table 6.5 provides some literature reported  $T_g$  values for various film formulations. Plasticization decreases the intermolecular forces between polymer chains and, consequently, reduces  $T_g$  values [73].

Measurement of T by DSC in starch samples is difficult since the change of heat capacity or the signal on heat flow are usually weaker than the corresponding conventional polymers. For acetylated based materials, T values of plasticized films were around 30% lower than those of unplasticized ones, indicating the well-known effect of glycerol on starch matrixes.

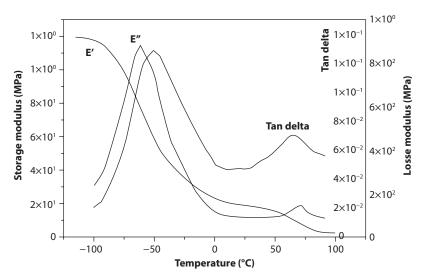
Film formulation	Glass tran	sition temperature
	Tg value (°C)	Method <sup>a</sup> and reference
Yam starch	48.0	DSC [18]
	44.2	TMA [18]
Yam starch plasticized with glycerol	12.2	DSC [18]
	10.9	TMA [18]
Acetylated corn starch	71.7	DSC and DMA [74]
Native and acetylated corn starch blend	71.5	DSC and DMA [74]
Gluten protein plasticized with glycerol	68.0	DMA [75]
Gelatin plasticized with sorbitol	56.5	DSC [76]
Chitosan (depending of water con- tent and acetylation degree)	-23.0 to 67.0	DSC and DMTA [40]
Pectin (regardless the methyl esteri- fication degree)	35.0	DSC [77]

 Table 6.5 Glass transition temperature (Tg) of films with different compositions.

<sup>a</sup> DSC = differential scanning calorimetry, TMA = thermomechanical analysis and DMA = dynamic mechanical thermal analysis.

Dynamic mechanical analysis (DMA) is an alternative method that can be applied to determine relaxation processes associated with glass transition temperatures ( $T_g$ ). This method is based on the determination of storage (E') and loss moduli (E''), as well as tan  $\delta$  as functions of temperature. E'; the elastic response of the material is related to the mechanical energy stored per cycle when the sample is subjected to a deformation. E'', the viscous response, is related to the dissipated energy as heat per cycle when the sample is deformed. Loss factor is defined as tan  $\delta = E''/E'$ , d being the angle between the in-phase and out-of-phase components of the modulus in the cyclic motion. Temperatures of the relaxation processes associated with glass transition temperatures were determined through the inflexion point of the storage modulus E' curve, as well as the maximum peak in both the loss modulus E'' and tan  $\delta$  curves [78].

Assays were carried out in a dynamic-mechanical thermal equipment Q800 (TA Instruments, New Castle, USA) with a liquid nitrogen cooling system, using a clamp tension. Multifrequency sweeps at fixed amplitude from -100 to 100°C at 2°C/min were carried out. E' and E'' moduli and tan  $\delta$  curves as a function of temperature were recorded and analyzed



**Figure 6.13** DMA spectra of acetylated corn starch films with 1.5% w/w glycerol. Dependence of E' (storage modulus), E'' (loss modulus) and tan  $\delta$  with temperature at a constant frequency of 3 Hz.

using Universal Analysis 2000 software. The linear viscoelastic range was around 12  $\mu$ m amplitude, thus, frequency sweep assays as a function of temperature were performed at constant amplitude of 5  $\mu$ m.

Figure 6.13 shows E', E'' and tan  $\delta$  curves of the acetylated starch, and it can be observed that their dynamic-mechanical response show two relaxation peaks. Similar behavior was observed for native corn, ahipa and cassava starch films. Several authors stressed that starch-glycerol mixtures are partially miscible systems, giving rise to a starch-rich phase and another phase rich in glycerol [20,42,74,79-80]. Likewise, Zhang and Han [25] stressed that glycerol miscibility in starch matrix is limited and depends on plasticizer concentration. Thus, dynamic-mechanical patterns of plasticized film show two relaxations, one located around -50°C, associated with the glass transition of the plasticizer-rich phase, and the other about 60°C, attributed to the starch-rich phase (Figure 6.13). A transition at around -50°C showed better definition with a higher associated intensity change than that of about 60°C. Our results are in agreement with those reported by the work of Jiang et al. [81] on thermoplastic acetylated tapioca starch films. A similar trend was also reported by other authors for films formulated with native starches from different sources such as barley [82], waxy maize [20], pea [83], mungbean [84], cassava [85] and cara [86] roots. This tendency was also reported for plasticized protein films [87].

 $-44.96 \pm$ 

0.01

 $-48.5 \pm 3.3$ 

 $-52.2 \pm 0.3$ 

 $42.9 \pm 6.9$ 

 $38.1 \pm 7.0$ 

 $48.3 \pm 1.4$ 

determined by 1	DMA (frequency:	10 Hz; amplitud	e: 5 μm).	
Plasticized	]	Relaxation tem	peratures (°C)	
film composition	Gly	cerol-rich phas	e	Starch-rich phase
	Inflexion of storage modu- lus (E')	Maximum of loss modulus (E")	Maximum of tan δ	Maximum of tan δ

 $-58.81 \pm 0.08$ 

 $-58.0 \pm 1.5$ 

 $-61.1 \pm 4.1$ 

**Table 6.6** Relaxation temperatures associated with the glass transition of the glycerol and starch-rich phases of starch films plasticized with 1.5% w/w glycerol determined by DMA (frequency:10 Hz; amplitude:  $5 \mu m$ ).

\* value ± standard deviation

Ahipa

Cassava

Corn

 $-59.9 \pm 1.7^{*}$ 

 $-61.0 \pm 3.4$ 

 $-60.92 \pm 0.01$ 

Dynamic-mechanical patterns of unplasticized films exhibited a single relaxation, in comparison with those containing glycerol. Biliaderis *et al.* [88] stressed that systems based on polymer-water presented only one transition.

Glycerol addition significantly decreased (p < 0.05) the relaxation temperature of the starch-rich phase, making this effect more marked in native starch films. These results are in agreement with the well-known effect of plasticizer on glass transition temperatures [50,88].

Table 6.6 shows the relaxation temperatures of the glycerol-rich phase; for ahipa starch film this relaxation occurs at higher temperatures compared to the cassava and corn ones. Also taken into consideration is the fact that the glass transition temperature, T<sub>g</sub>, of pure glycerol is located at -78°C [89]. Similar results were reported by García *et al.* [20] working on cassava and waxy maize starch films. A similar trend was also reported by other authors for films formulated with native starches from different sources such as barley [90], waxy maize [20], pea [83], mungbean [84], corn [74], cassava [85] and cara [86] roots. This tendency was also reported for plasticized protein films [87].

## 6.2.2.5 Barrier Properties

Barrier properties ultimately determine the films ability to improve the storage life of food products. Water vapor and gas permeability is commonly measured and it is strongly related to film structure, since permeants generally move through the amorphous film zones. Film components,

especially plasticizers, affect both barrier and mechanical properties, because they modify film structure, chain mobility and the permeants' diffusion coefficients.

## 6.2.2.5.1 Water Vapor Permeability (WVP)

Determination of WVP is highly dependent on measurement conditions such as temperature and the gradient of water vapor pressure. Water vapor permeability testing of films may be conducted according to method E96-95 [91] that includes some modifications introduced by Gennadios *et al.* [47]. Since barrier thickness strongly affects water vapor transport through the film matrix, it is necessary to consider film thickness in WVP calculations. In addition, WVP determinations can be performed using PERMATRAN equipment, a specific instrument developed by MOCON to analyze synthetic film materials.

Films without plasticizer often yield significantly higher WVP values than those with plasticizer (Table 6.7), which is attributed to the presence of pores and cracks. These results could be related to structural modifications of the starch network produced by the presence of plasticizer, as well as to the glycerol hydrophilic character which favors water molecules absorption/desorption, promoting the permeability. Glycerol interferes with the polymeric chains association, decreasing the network rigidity; thus a less ordered and compact structure is achieved, decreasing WVP [18]. A similar tendency were reported by Galdeano *et al.* [92] for oat starch films plasticized with glycerol (20g/100g starch). Sorbitol generally resulted in lower WVP values compared to glycerol in plasticized starch-based films (Table 6.7). McHugh and Krochta [93,94] reported similar results for alginate and pectin films using the same plasticizers at similar concentrations.

Amylomaize films, with higher amylose content, denser matrix structure and higher degree of crystallinity than those of standard corn starch, also exhibited relatively lower WVP values. A similar trend has been observed by others [95–97]. However, the amylose content effect on the WVP of starch film was minimized by the incorporation of sunflower oil into the coating formulation (Table 6.7). The addition of sunflower oil significantly decreased the WVP of starch-based films and coatings. Baldwin *et al.* [98] reviewed the lipid effects on other non-starch composite films. As water vapor transfer generally occurs through the hydrophilic film portion, WVP is dependent on the hydrophilic-hydrophobic ratio of the film components [99]. In general, WVP increases with both lipid polarity and degree of unsaturation/branching, though water absorption properties of the films polar components must also be considered [45].

Film formulation		$\begin{array}{c} \text{Water vapor permeability} \times \\ 10^{11} \left(g \; m^{-1} \; sec^{-1} \; Pa^{-1}\right) \end{array}$
Cornª	Without additives	$36.8\pm22.4^{\rm f}$
	Glycerol (G) <sup>c</sup>	$25.7 \pm 10.4$
	G + Sunflower oil (SO) <sup>d</sup>	$19.2 \pm 4.7$
	Sc	$17.5 \pm 1.4$
	S + SO <sup>d</sup>	$12.2 \pm 1.1$
Amylomaize <sup>a</sup>	Without additives	26.2 ± 13.9
	G <sup>c</sup>	$21.4 \pm 7.5$
	G + SO	$17.6 \pm 3.7$
	S <sup>c</sup>	$12.1 \pm 1.5$
	S + SO	$9.7\pm0.8$
Ahipa <sup>b</sup>	Without additives	$26.0 \pm 1.0$
	Ge	$16.0 \pm 2.0$
Cassava <sup>b</sup>	Without additives	$16 \pm 1.0$
	G <sup>e</sup>	$14 \pm 1.0$
Acetylated corn <sup>b</sup>	Without additives	$13.3 \pm 0.2$
	Ge	$1.6 \pm 0.1$

**Table 6.7** Effect of formulation on water vapor permeability of starch-basedfilms.

<sup>a</sup> Corn starch and amylomaize concentration = 20g/L, <sup>b</sup>Ahipa, cassava and acetylated corn starch concentration: 50g/L, <sup>c</sup> Glycerol and sorbitol concentration = 20g/L, <sup>d</sup> SO = sunflower oil (2g/L), <sup>e</sup> Glycerol concentration = 15g/L, <sup>f</sup> Value ± standard deviation

The WVP values for corn, cassava and ahipa starch films are similar to those reported by other authors for different starch types [100–104]. The WVP reduction caused by the addition of glycerol was 38, 9 and 65% for ahipa, cassava and corn starch films, respectively. The lower WVP reduction for cassava starch films could be attributed to the high apparent viscosity of its filmogenic suspensions that led to the development of more cohesive matrixes, with good barrier properties, even without plasticizer addition.

Lower WVP value was obtained for plasticized acetylated corn starch films due to the hydrophobic character of the substituent (Table 6.7). The addition of plasticizer was necessary to maintain film integrity, reducing film fragility and avoiding pores and cracks. Table 6.7 shows that glycerol incorporation reduces by 88% the WVP of acetylated corn starch films.

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The WVP of yam starch film is lower than that of many edible, biodegradable films such as wheat gluten plasticized with glycerol and amylose and hydroxypropylmethylcellulose containing plasticizer and oil [105]. In general, starch exhibit lower WVP (an order of magnitude) compared both to protein films and other polysaccharide-based films reported in literature [54,93,94,106–109]. In comparison to synthetic polymers, starch films have WVP values similar to those of cellophane, but higher than low density polyethylene (LDPE), the most common synthetic film [110].

#### 6.2.2.5.2 Gas Permeability (CO<sub>2</sub> and O<sub>2</sub>)

Film permeability to  $CO_2$  and  $O_2$  measurement is essential to understanding quality and physiological aspects of coated fruit products during storage. Oxygen permeability can be measured using commercial instruments, such as the OXTRAN equipment developed by MOCON. In addition,  $CO_2$  and  $O_2$  permeability of films can be assessed by the accumulation method using a specially designed cell [10,54,111]. This quasi-static method is based on the measure of gas diffusing through a film, which is quantified by gas chromatography. As it was previously described for WVP determinations, calculated values for gaseous permeability must account for film thickness.

Films' structural integrity conditions barrier properties, thus, unplasticized starch films exhibit much higher  $CO_2$  and  $O_2$  permeability and also higher standard deviation coefficients than the same formulations containing plasticizers (Table 6.8). This result was attributed to the presence of pores within unplasticized matrixes, resulting in a lack of film integrity, as determined by SEM [10,106]. Starch films with sorbitol exhibit lower oxygen permeability values than those formulated with glycerol (Table 6.8). Sorbitol combined with an amylomaize film matrix provided the lowest gas permeability values for all materials tested (Table 6.8). McHugh and Krochta [93,94] found similar results working on milk and whey protein films.

Table 6.8 shows that  $O_2$  permeability of starch-based films were much lower than those of  $CO_2$ , indicating a variable permeability of these films to select gases. This effect can be attributed to a higher solubility of  $CO_2$  than  $O_2$  in film matrix [93]. Similar results were obtained by Arvanitoyanis *et al.* [112] while working with potato and rice starch films. Further, addition of lipid, which is necessary to reduce water vapor permeability, maintained the selective gas permeability properties of the starch-based films (Table 6.8).

Synthetic film materials, such as LDPE, show lower gas permeabilities  $(2.16 \times 10^{-11} \text{ and } 9.45 \times 10^{-11} \text{ cm}^3 \text{ m}^{-1} \text{ sec}^{-1} \text{ Pa}^{-1} \text{ for O}_2 \text{ and CO}_2$ , respectively)

Starch base	Additives	$\begin{array}{c} \text{CO}_{2} \text{ permeability} \\ \times 10^{10} \ (\text{cm}^{3} \text{ m}^{-1} \\ \text{sec}^{-1} \ \text{LSD}_{0.05} = 1.63 \end{array}$	O <sub>2</sub> permeability × 10 <sup>10</sup> (cm <sup>3</sup> m <sup>-1</sup> sec <sup>-1</sup> ) LSD <sub>0.05</sub> = 1.03
Corn	_	292.1 ± 138.9°	$15.92 \pm 2.99$
	Glycerol <sup>a</sup>	$56.9\pm9.7$	$4.61\pm0.51$
	Glycerol + SO <sup>b</sup>	$58.7 \pm 5.8$	$3.83\pm0.76$
	Sorbitol <sup>a</sup>	$41.9\pm8.1$	$2.48\pm0.32$
	Sorbitol + SO	$47.2 \pm 6.5$	$3.77\pm0.03$
Amylomaize	_	$280.5 \pm 73.7$	$26.45\pm2.48$
	Glycerol	$38.5 \pm 12.8$	3.21 ± 0.19
	Glycerol + SO	$43.9\pm9.0$	$2.36\pm0.04$
	Sorbitol	29.6 ± 4.6	$2.28\pm0.26$
	Sorbitol + SO	$34.3 \pm 2.1$	$2.18\pm0.04$

 Table 6.8 Film formulation effect on gas permeability of starch-based films.

 $^{\rm a}$  Glycerol and sorbitol concentration = 20g/L;  $^{\rm b}$  SO = sunflower oil (2g/L);  $^{\rm c}$  Value  $\pm$  standard deviation

**Table 6.9** Effect of plasticizer and starch type on  $CO_2$  permeabilities of starch-based films.

Starch base	Plasticizer	$CO_2$ permeability × 10	<sup>9</sup> [cm <sup>3</sup> /m sec Pa] <sup>a</sup>
	(20 g/L)	Initial time <sup>a</sup>	Stored samples <sup>b</sup>
Corn	_	29.21 ± 13.89°	8.90 ± 1.28
	Glycerol	$5.69 \pm 0.97$	2.76 ± 0.55
	Sorbitol	$4.19 \pm 0.81$	$2.42\pm0.46$
Amylomaize	_	$28.05 \pm 7.37$	$7.71 \pm 1.40$
	Glycerol	3.85 ± 1.28	$2.28 \pm 0.33$
	Sorbitol	$2.96 \pm 0.46$	$1.82 \pm 0.15$

 $^{\rm a}$  At standard pressure and temperature conditions;  $^{\rm b}$  Stored 20 days at 20°C and 63.8% relative humidity;  $^{\rm c}$  Value  $\pm$  standard deviation

with regard to starch-based films. However, LDPE has a relatively low  $CO_2$  to  $O_2$  permeability ratio ( $\approx$ 4), compared to an average ratio of 13 for starch-based films [113–115]. Cuq *et al.* [116] compared the  $CO_2$  to  $O_2$  permeability ratios of several synthetic and edible films, and reported that edible films show higher selectivity than synthetic ones, with ratios for edible films ranging from 8 to 30. Development of composite edible films and coatings with selective gas permeabilities could be very promising for

controlling respiratory exchange and improving the conservation of fresh or minimally processed vegetables [113–115].

Table 6.9 shows that the  $CO_2$  permeability of starch-based films decreased with increasing lengths of storage [51]. Gas and vapor permeabilities of films and coatings depend on several factors such as: i) the ratio of crystalline to amorphous zones, ii) polymeric chains mobility, and iii) specific interactions between the functional groups of the polymers and gases within the amorphous zones. Table 6.9 shows that  $CO_2$  permeability of starch-based films decreased with increasing lengths of storage [51]. Gaseous permeability measurements of starch stored films correlated with the increase of crystallinity degree, reported by DSC and XRD (Figure 6.11). According to Donhowe and Fennema [117], film permeability increases by decreasing crystalline to amorphous zone ratio, since permeation occurs through the amorphous zone.

## 6.2.2.6 Mechanical Properties

Films mechanical properties are dependent on additive-matrix interactions, and are also strongly affected by physical, chemical and environmental conditions, which influence material stability and flexibility. The mechanical performance of films is usually characterized by the deformation at break, tensile strength and elastic modulus according to the ASTM D882-91 method [118] and can be determined using a texturometer or an Instron universal machine. These parameters are related to the films stretching ability. It is well known that the films mechanical properties are strongly affected by environmental conditions during their production, storage and use. The aging phenomena occurring during the useful lifetime

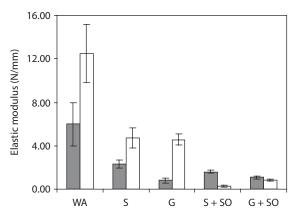


Figure 6.14 Stress-strain curves of amilomaize starch films.

Film type		Mechanical proper	rties
		Tensile strength (MPa)	Elongation at break (%)
Biodegradable	CSª	$47.4 \pm 1.5$	3.6 ± 0.5
	CS + G	$7.1 \pm 0.4$	$22.5 \pm 4.2$
	Acetylated corn	$60.94 \pm 0.76$	$1.89 \pm 0.15$
	Acetylated corn + G	$41.85 \pm 2.44$	$5.44 \pm 0.26$
Synthetic	Cellophane <sup>b</sup>	85.8 ± 8.9	$14.4 \pm 2.4$
	LDPE <sup>c</sup>	$16.2 \pm 4.0$	68.7 ± 14.9
	HDPE <sup>c</sup>	$27.8 \pm 3.2$	$150.0 \pm 18.5$

**Table 6.10**Comparison of the mechanical properties of films based on nativeand acetylated corn starch with commercial synthetic films.

 $^{\rm a}$  CS: corn starch at 5 g/100g;  $^{\rm b}[123];\,^{\rm c}[110]$ 

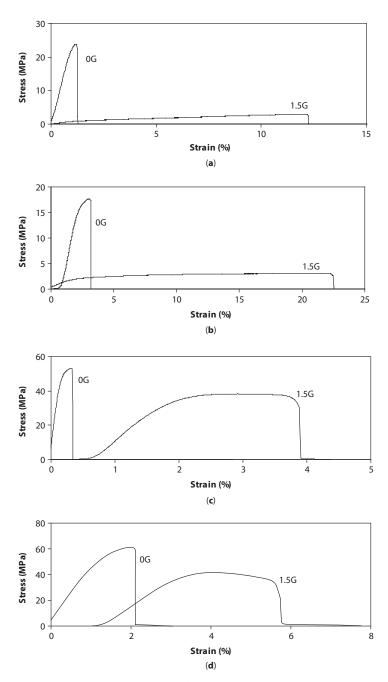
LDPE: Low density polyethylene and HDPE: high density polyethylene

of films also causes great losses to their mechanical properties, particularly in regard to film elongation.

Plasticizers interfere with polymeric chains association, facilitating their slipping and thus decreasing the rigidity of the network, producing a less ordered film structure. In the case of amylomaize films, high values of elastic modulus were obtained (Figure 6.14), which were attributed to their high amylose content. According to Garcia *et al.* [54], plasticizer-matrix interaction showed similar trends for both corn starch and amylomaize films, though plasticized corn starch films were more flexible than those of amylomaize. The combination of lipid and plasticizer addition increased film flexibility, and reduced the effect of starch type on film mechanical properties.

Stress-strain curves for cassava, ahipa and corn starch (CS) without plasticizer showed a typical pattern of brittle materials, as can be observed in Figure 6.15 [119,120]. Plasticized films exhibited stress-strain behavior of ductile polymers compared with unplasticized films (Figure 6.15, Table 6.10). Starch films plasticized with glycerol exhibited the most flexible behavior [121]. Similar results were obtained by Laohakunjit and Noomhorm [122] and Mali *et al.* [120] for cassava starch films plasticized with glycerol or sorbitol.

Films without glycerol were more brittle compared to those with plasticizer; being that unplasticized corn starch films are the most resistant and less flexible (Table 6.10). It could be related to the higher amylose content of corn starch; there is broad agreement in the literature regarding the



**Figure 6.15** Stress-strain curves of starch films without (0 G) and with 1.5% w/w glycerol (1.5 G): (a) ahipa starch; (b) cassava starch, (c) corn starch and (d) acetylated corn starch.

positive effect of amylose content increase on the elastic modulus of starch films [6,101,123-124]. According to Rindlav-Westling et al. [125], amylose network structure is very stable, with strong molecular orientation, forming denser films than the amylopectin one. Besides, Zobel [126] found that linear amylose molecules formed strong films, whereas branched amylopectin-based films were weak and brittle. When glycerol was incorporated the mechanical behavior of these materials changed considerably (Figure 6.15), decreasing tensile strength, as well as elastic modulus; while elongation at break increased significantly (p < 0.05; Table 6.10). When plasticizer is added, starch chains proximity is reduced, thus under tensile forces movements of starch chains are facilitated [92]. Similarly to unplasticized materials, corn starch films with glycerol remained more resistant and less flexible than those of tuberous starches (Table 6.10). It should be taken into account that the mechanical behavior of films is related to the network compaction degree, which is influenced by the amylose:amylopectin ratio, the chains' characteristics and glycerol interactions.

Tensile strength of films containing acetylated starch were significantly (p < 0.05) higher than those of native starch ones, regardless of the addition of glycerol (Tables 6.10). Although acetyl groups interfere with the alignment of the chains, they led to the development of a more resistant matrix due to the reinforcement by hydrogen bonds between aligned polymeric chains. Several authors have reported that structural modification of starch matrix is a useful tool to improve films' mechanical strength and barrier properties [15,32,83,86]. Young's modulus showed a similar trend to the tensile strength (Table 6.10). The addition of glycerol improved mechanical behavior, increasing significantly (p < 0.05) elongation at break.

Likewise, Table 6.10 compares mechanical properties determined for both biodegradable and synthetic films under identical test conditions. Tensile strength values for biodegradable films were in the range of those for LDPE and HDPE, but were lower than the ones corresponding to cellophane. However, synthetic polymers like LDPE and HDPE exhibited much greater values for elongation at break. Similar results were reported for synthetic films by Cunningham *et al.* [127].

## 6.2.3 Specific Properties Analyzed in Native and Acetylated Corn Starch Films: Heat Sealing Performance and Analysis of Failure Modes

The heat sealing capacity of flexible films is a critical feature and determines the integrity of the package. Zip quality depends on processing conditions such as temperature, time and pressure, as well as previous film treatments. When molecular interaction between individual layers is enough to destroy the interface and lead to a new homogenous layer, a good quality zip is obtained [128].

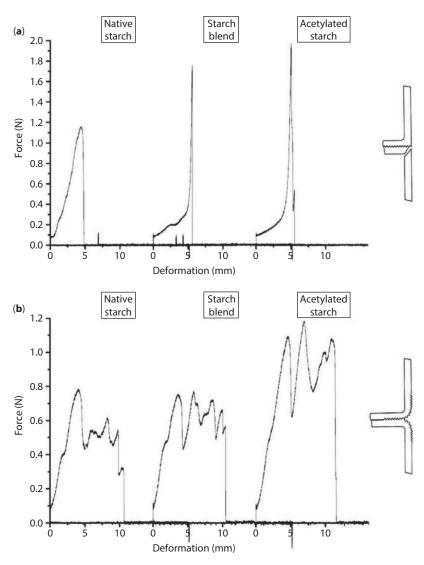
Numerous sealing techniques are available, including bar, band, impulse, wire or knife, ultrasonic, friction, gas, contact, hot-melt, pneumatic, dielectric, magnetic, induction, radiant and solvent sealing methods [129]. Selection of heat sealing type depends mainly on the polymeric film structure, packaging and product. Regardless of the type used, it should assure the mechanical resistance and packaging integrity, preventing microorganisms entrance and maintaining its barrier properties. Sealing strength, which is a quantitative measurement used in process validation and control, is influenced by film thickness. Besides, the knowledge of the failure mode of a heat sealed material is critical since it conditions packaging performance and describes how the two sealed surfaces are separated during the resistance assays. Different failure modes (adhesive, cohesive, delaminated, rupture near to the zip, rupture far from the zip, stretching and adhesive plus stretching) were described by ASTM F88-00 standard method [130].

Starch-based films are sealed by impulse sealing technique, which is widely used to zip flexible synthetic films [129]. In this technique, jaws are heated to fusion temperature by a short powerful electric impulse. Impulse wire sealing was selected over impulse bar sealing since it allows cooling the zip, enhancing its strength, before the jaws were opened [129,131].

Heat sealing ability of the developed starch films was evaluated and the best zip quality was achieved at  $154.3 \pm 8.5$  C during  $1.84 \pm 0.01$  s for all film formulations. Figure 6.16 shows the typical curves obtained from heat sealing resistance assays as well as the failure modes associated. Unplasticized films exhibited a rupture near the zip, while plasticized ones presented adhesive failures (Figure 6.16.) Acetylated starch films exhibited the higher values of the maximum traction resistance compared to native ones, while an intermediate behavior was recorded for the blend (Figure 6.17). According to Lacroix [132] the presence of functional groups such as hydroxyl, aldehyde and carboxyl acids are responsible for the different adhesion strengths of the films.

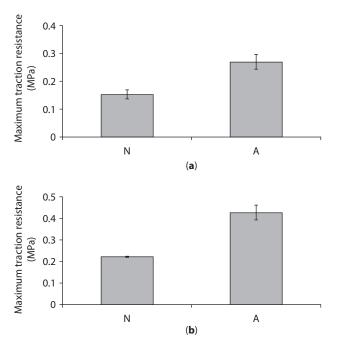
A similar effect in polyethylene films was described by Possart and Deckhoff [133]; the enhancement of the seal strength was attributed to the increase in chain interaction due to the incorporation of nitrogen- and oxygen-containing functional groups.

Glycerol addition did not modify this tendency since plasticized acetylated starch films exhibited statistically (p < 0.05) higher media heat sealer



**Figure 6.16** Typical curves of heat sealing resistance and the associated failure modes of films based on acetylated, native corn starch and their blend; (a) films without plasticizer and (b) films plasticized with 1.5% w/w glycerol.

resistance values than those of native ones (Figure 6.17). Besides, the necessary energy to cause adhesive failure of native and starch blend films were comparable, while acetylated ones showed the highest value. Again, this was attributed to the higher resistance of acetylated matrix due to the structure reinforcement by the incorporation of the acetyl groups.



**Figure 6.17** Heat sealing resistance of films based on acetylated (A), native (N) corn starch: (a) maximum traction resistance of unplasticized films and (b) media heat sealing resistance of 30% (w/w) glycerol plasticized films and the necessary energy to cause adhesive failure.

# 6.3 Development of Active Starch Films Containing an Antimicrobial Agent (Potassium Sorbate)

The food industry is focusing their efforts towards offering the consumers safer, more nutritious and higher quality products. Microbial contamination of food products causes serious diseases and consequent economic losses [134]. Thus, addition of bactericidal agents or growth inhibitors into food formulation by spraying or immersion methods has been employed to overcome food contamination. However, direct application of the antimicrobial agents has some limitations since they can be neutralized, evaporated or diffused rapidly and inadequately into the food bulk, reducing their effective concentration on the surface [135,136]. In this context, a current trend with good prospects consists of the incorporation of the additives to food packages, improving their functionality [137,138]. Active agents are added to the film matrix and slowly released to the food surface, where they remain at a high concentration for a long time [139]. The effectiveness

of the addition of potassium sorbate to plasticized corn starch films to prevent microbial growth on a food product surface was studied. Sorbate controlled release from the polymeric matrix to a semisolid medium was evaluated by López et al. [13]. Active starch films with glycerol and potassium sorbate were obtained by casting. Aqueous suspensions (5% w/w) of native and acetylated corn starch were gelatinized at 90°C; then, glycerol as plasticizer (1.5% w/w) and potassium sorbate (PS) as antimicrobial agent (0.1-0.5% w/w) were added. Filmogenic suspensions with pH adjusted at 4.5 were also prepared by adding 5 M citric acid in order to increase the preservative effect of PS, since its undissociated form is the effective one. For further analysis and discussions, plasticized films without active agent were used as controls. The PS incorporation did not modify the filmogenic capacity of starch formulations, obtaining homogeneous films and easily removable from the casting plates. It was determined that additive concentration diminished approximately 21% during film storage due to sorbate degradative oxidation. Several authors stressed that this reaction depends mainly on storage conditions and the presence of other additives [140,141].

The PS minimum inhibitory concentration (MIC) was determined by the method proposed by Fajardo *et al.* [142] using a cheese sample with high humidity content (55%), elaborated with full cream milk and acidified with lactic acid bacteria. The lowest additive concentration which did not allow visual observation of fungi growth on cheese surface was 0.3% w/w. Stanojevic *et al.* [143], investigating antimicrobial effects of PS on selected food- spoiling bacteria and fungi, stressed that MIC depends on the kind of preservative and the microorganism taxonomic characteristics.

Active films antimicrobial activity was evaluated testing the following microorganisms: S. aureus, Candida spp., Salmonella spp. and Penicillium spp, since they are mainly responsible for foodborne diseases [13]. They were cultivated from stock vials in Tryptic Soy Broth (TSB) and incubated at 37°C during 12 h to reach a concentration of 10<sup>8</sup>-10<sup>9</sup> CFU/mL. Besides, diluted inocula were prepared to reach a concentration of 107-108 CFU/mL. The agar diffusion method described by Pranoto et al. [135] was followed, using the previously described inocula, incubating samples at 37°C. For S. aureus, Candida spp. and Salmonella spp. visual observations and film inhibition zone at different incubation times (24, 48 and 94 h) were carried out. For *Penicillium spp.*, observations as well as inhibition zone measurements were performed at 48 h and at 8 days of storage. To determine the inhibition zones, sample photographs were taken at different storage times and they were processed with the software GIMP 2.2 (GNU Image Manipulation Program). Figure 6.18 corresponds to the photographs of the inhibition zones observed for Candida spp. and Penicillium spp. In general, microbial growth inhibition and the effect of the formulation pH were better observed working with the most diluted inoculums  $(10^7-10^8 \text{ CFU/mL})$ . Active starch film formulations based on native and acetylated corn starch inhibited *Candida spp.* growth and a positive effect of the pH adjustment to 4.5 was observed since the corresponding inhibition zones presented the largest diameters (Table 6.11).

It was not possible to measure the inhibition zones for *Penicillium spp.*; therefore a visual inspection of the microbial growth and a qualitative description were done. For films based on native starch, when concentrated inocula were seeded, fungi development was not observed, regardless of the formulation pH (Figure 6.18). In the case of acetylated films, although fungi grew, the pH adjustment effect was evident (Figure 6.18). Sofos and Busta [144] have extensively described how potassium sorbate inhibits the development of a great number of bacteria (gram positive and negative, catalase positive and negative, aerobic and anaerobic, mesophilics and psycrotrophics). Active film inhibitory action on S. aureus and Salmonella spp. was evaluated [13]. The selection of these microorganisms was based on their pathogenesis and their amenability on some diseases transmitted by foods. Both bacteria are facultative anaerobic, being S. aureus gram positive and Salmonella spp. gram negative. Native starch films with potassium sorbate inhibited S. aureus growth, being that this effect was 34% higher for films with pH = 4.5. Pranoto *et al.* [135] reported that chitosan films containing potassium sorbate also presented antimicrobial effectiveness against this microorganism, evaluated by the agar diffusion method. In the case of Salmonella spp. similar results were observed. Besides, pH adjustment increased by 22% the inhibitory zone diameter for starch films based on native starch. Active acetylated starch films were only able to inhibit the development of both bacteria in the contact zone between the film and the culture medium, regardless of the suspension pH.

# 6.4 Advances in Starch Films Production Using Non-Casting Methods: Thermocompression and Blown Extrusion

In order to convert starch into films, the casting technique is the most widely used procedure in research works [15,28,29,74,145,146]. Even though this is a useful technique at laboratory scale, it must be taken into account that this method involves the gelatinization of an aqueous starch suspension and its subsequent dehydration under controlled conditions,

	Inoculum 10	0 <sup>8</sup> –10 <sup>9</sup> UFC/mL	Inoculum 1	0 <sup>7</sup> -10 <sup>8</sup> UFC/mL
	pH non- adjusted	pH=4.5	pH non- adjusted	pH=4.5
	Native	e corn starch films	-1.5G-0.3KS	
Candida spp. (1 day)	0.9	0.0	0	0
Penicillium spp. (8 days)	6			
	Acetylat	ed corn starch fil	ms-1.5G-0.3KS	
Candida spp. (1 day)			P	6
Penicillium spp. (8 days)				

**Figure 6.18** Inhibition zones development of *Candida spp*. and *Penicillium spp*. in starch films with glycerol (1.5% w/w) and potassium sorbate (0.3% w/w PS).

**Table 6.11** Inhibition zones measurements of *Candida spp.* in corn starch films with 1.5% w/w glycerol (1.5G) and 0.3% w/w potassium sorbate (0.3KS).

Film		Inhibition	zone (mm)	
composition	Inoculum 10 <sup>8</sup>	-10 <sup>9</sup> UFC/mL	Inoculum 10 <sup>7</sup>	-10 <sup>8</sup> UFC/mL
	pH non-adjusted	pH = 4.5	pH non-adjusted	pH = 4.5
	non-adjusted		non-adjusted	
N-1.5G-0.3KS	$13.55\pm0.12$	$15.71\pm0.63$	$42.08 \pm 1.14$	$43.53 \pm 1.07$
A-1.5G-0.3KS	10	10	36.38 ± 1.95	$43.25 \pm 0.36$

N: native corn starch; A: acetylated corn starch; 1.5 G: 1.5 g glycerol/100g; 0.3 KS: 0.3 g potassium sorbate / 100g.

being considered as an energy-consuming procedure. Besides, industry requires high levels of biodegradable film production, so the scale-up of the obtaining process employing the existing processes for synthetic materials is indispensable [147]. In this context, the extrusion method followed by blowing or thermo-compression molding is a viable alternative due to its energy efficiency combined with its high productivity [28,147,148,149].

Thermoplastic starch (TPS) is a relatively new concept and, actually, it is one of the main research hints for biodegradable materials manufacturing [150–154]. Starch is not a real thermoplastic material, but when it is processed with plasticizers under high temperature and mechanical forces, granules suffer destructuring and starch melts and flows [152–157].

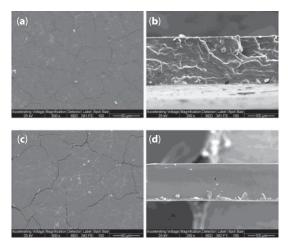
Thermoplastic starch can easily be adapted to different processes employing standard equipments used for synthetic polymers, such as extrusion, blowing, injection and compression molding [1,154,158]. This possibility would enhance the commercial potential of biodegradable films since it is feasible working in a continuous system with ready control of process variables such as temperature, moisture, and size/shape. Nowadays, there are a wide variety of available products obtained by processed TPS from different native starches, like disposable bags, containers, vessels, forks, knifes and garbage bags [153,159].

## 6.4.1 Thermoplastic Corn Starch by Thermocompression

Starch can be converted into a thermoplastic material by its processing under high shear stress and high temperatures in a plasticizer presence [160,161]. Thus, starch semicrystalline granular structure is disrupted and the polymer melts [1].

Films based on thermoplastic corn starch were obtained by thermocompression and their structure and properties were studied. Blend compositions as well as processing conditions were set following literature data for analogous systems processed by thermocompression [148].

Mixtures of native corn starch, glycerol (30% w/w) and distilled water (25 and 45% w/w) were prepared. Blend composition was expressed in g per 100 of starch and they were named 10:3:2.5 and 10:3:4.5, respectively. Samples were processed in a Brabender Plastograph (Brabender, Germany) at 140°C and 50 rpm for 15 min. Processed mixtures were removed from the mixing chamber, triturated and conditioned at 25°C and 60% relative humidity (RH) in order to improve their future processability. Films were obtained by thermocompression using a hydraulic press using the following processing conditions: 150 kg cm<sup>-2</sup> at 140°C during 6 min.



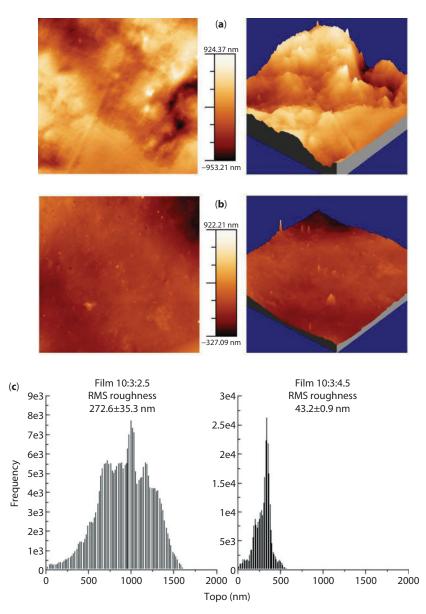
**Figure 6.19** Surfaces and cross-section SEM micrographs of films obtained by thermocompression based on thermoplastic corn starch with 30% w/w glycerol and 25 (a and b) and 45% w/w (c and d) water.

The obtained materials that resulted were homogenous, presented good integrity, adequate handling characteristics and their thickness varied between 178 and 223  $\mu$ m.

The films homogeneity and appearance were examined by visual observation, as well as by SEM with a JEOL JSM 6360 electron microscope (Japan). Figure 6.19A and B correspond to SEM micrographs of TPS films obtained from the mixture 10:3:2.5. Film surface showed the appearance of few unmelted starch granules and some small pores (Figure 6.19a), while its cross-section presented an irregular structure (Figure 6.19b). On the other hand, Figure 6.19c and d shows SEM micrographs of TPS materials corresponding to the formulation 10:3:4.5. Film surface again showed some unmelted starch granules, however the presence of cracks that resulted were lower than for formulation 10:3:2.5 (Figure 6.19c). Film cross-section evidenced a development of homogeneous structure due to water content increase in the formulation (Figure 6.19d). In all cases, a low film thickness variation was observed, which demonstrates the effective-ness of the thermocompression method [42].

Topography and roughness surfaces of the starch films were evaluated using a multimode atomic force microscope Nanoscope V (Veeco Instruments). Figure 6.20a and b show the bi- and three-dimensional topographic images of the films obtained from the mixtures 10:3:2.5 and 10:3:4.5. Figure 6.20c shows the height profiles and the RMS roughness values corresponding to each formulation. Starch film obtained from the

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**Figure 6.20** Bi- and three-dimensional AFM images of films obtained by thermocompression based on thermoplastic corn starch with 30% w/w glycerol and 25 (a) and 45% w/w (b) water. (c): Height profiles and RMS roughness values.

**Table 6.12** Mechanical properties of films obtained by thermocompressionbased on thermoplastic corn starch with 30% w/w glycerol and 25 and 45% w/wwater.

Formulation	Elastic modulus (MPa)	Maximum tensile stress (MPa)	Elongation at break (%)
10:3:2.5*	166.3±12.2	3.82±0.14	32.77±2.41
10:3:4.5	146.6±13.3	3.46±0.34	37.61±2.17

\*% w/w acetylated corn starch:% w/w native corn starch:% w/w glycerol

mixture 10:3:2.5 had a smooth surface showing the globular structure of starch granules (Figure 6.20A). Vigneshwaran *et al.* [162] reported a similar result for starch films prepared by the solution casting method. On the other hand, films obtained from formulations with the highest water content presented less surface roughness (Figure 6.20B). This result is evident in the bi- and three-dimensional images and in the height profiles, as well as in the roughness parameters. Films 10:3:4.5 presented a RMS roughness value 84% lower than films 10:3:2.5 (Figure 6.20C).

In order to evaluate TPS films mechanical behavior tensile tests were performed in a universal Instron machine 3369 (USA). The TPS films mechanical properties are shown in Table 6.12. Elongation at break was the property most affected by water content increase in the formulation, registering an increment of around 14%. On the other hand, elastic modulus and maximum tensile stress values decreased approximately 12 and 9% with water content increase.

In conclusion, biodegradable films based on TPS were developed by thermocompression. The obtained materials that resulted were homogeneous and transparent. By SEM it was observed that an increase in water content in formulations led to the obtainment of materials with more homogenous and compact structure, as well as a significant decrease in film surface roughness. With respect to mechanical properties, it was observed that there was an increase in film flexibility with water content in TPS formulations.

# 6.4.2 Acetylated and Native Corn Starch Blend Films Produced by Blown Extrusion

The extrusion method followed by blowing or thermocompression molding is a viable alternative to produce starch films due to its energy efficiency combined with its high productivity [28,148,149]. In order to evaluate the

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Starch	Acetylated	Native corn	AS/NS	AS/NS Glycerol	Humidity con	Humidity content (% w/w)
formulation	corn starch (AS) (% w/w)	starch (NS) (% w/w)		(% w/w)	Blend (before processing)	Pellets
$1 (10:70:20)^{*}$	10	70	0.14	20	$17.77 \pm 0.16$	$10.49 \pm 0.32$
2 (80:5:15)	80	5	16	15	$15.00 \pm 0.17$	$7.70 \pm 0.25$
3 (75:5:20)	75	5	15	20	$17.81 \pm 0.23$	$10.50 \pm 0.36$
4 (15:70:15)	15	70	0.21	15	$15.10 \pm 0.08$	$7.88 \pm 0.23$
5 (45:37.5:17.5)	45	37.5	1.2	17.5	$16.51 \pm 0.20$	$9.30 \pm 0.06$
······ [+/ /0/*			[]]			

(% w/w acetylated corn starch:% w/w native corn starch:% w/w glycerol)

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possibility to develop TPS films by blown extrusion, mixtures of native and acetylated corn starches with glycerol were processed [163]. To optimize the formulations an experimental design for multicomponent mixtures was used. The advantage of this design is the possibility to evaluate the effects of the individual and combined variables through an experimentally delimited assay [164]. Assayed formulations are shown in Table 6.13; they were determined using Statistica software version 6.0, (StatSoft, USA).

Operating conditions should be selected taking into account the need to avoid starch degradation but allowing a complete starch plasticization, as well as a good material flow through the extruder barrel. In this particular case, 140°C was employed in the three heating zones of the extruder. The TPS pellets were obtained using a pilot extruder BGM ELR-25 (Brazil) equipped with a single screw of 250 mm in diameter and a 10-HP motor. A matrix containing six orifices of 2 mm in diameter was employed. It must be taken into account that the screw speed should generate enough torque to destroy starch crystalline structure, allowing its plasticization. To process the above-mentioned native-acetylated TPS mixtures, a screw speed of 40 rpm was used. The humidity content of the blends before they were submitted to the extrusion process, and the values corresponding to the pellets, are reported in Table 6.13. As can be observed, the moisture content of blends and pellets increased with glycerol concentration due to the plasticizer's hydrophilic character. Results corresponding to the blends were closer to those reported for Galicia-García et al. [165] for mixtures based on native starch (corn, potato and waxy corn) and phosphorylated corn starch blended with bagasse fiber, plasticized with glycerol (22%). Extrusion of blends caused a sample dehydration, decreasing the humidity content 45% on average. Avérous et al. [166] also reported a decrease (~ 5%) in the water content of blends based on wheat starch and natural cellulose fibers, plasticized with glycerol, after they were being processed.

The blowing process was used to obtain the corresponding films. The previously described extruder was fed with TPS pellets to obtain starch film tubes of approximately 15 cm in diameter. Pellets obtained from the different tested formulations showed adequate processability to form films by blown extrusion, supporting the tension exerted by rolling and the air flow pressure without showing a tendency to tear. The blowing process conditions employed led to the development of homogeneous films without bubbles, regardless of the TPS formulation (Figure 6.21). Screw rotation speed was 40 rpm; temperature setting along the extruder and die temperature was  $120/120/120 \pm 2^{\circ}$ C. Móscicki *et al.* [167] stressed that it is not advisable to submit TPS materials at blown temperatures below  $120^{\circ}$ C since some residual pellets could appear on film surfaces.

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Figure 6.21 TPS films obtained by blown extrusion.

It is well known that water is considered a natural plasticizer for starch matrixes and can be regarded as a process aid since the melt viscosity is lowered with increasing water content. However, in this study no extra water was incorporated into the formulations since this one restricts the upper processing temperature because steam generation in the material leads to bubbles and foaming, which is not desirable in film blowing [147]. The obtained materials presented a certain stickiness, which disallowed that TPS films could be winding when they emerged from the die; this problem might be overcome, maintaining the bubble blown till it reaches ambient temperature. Flores *et al.* [28] and Thunwall *et al.* [147] also reported the same inconvenience with respect to the grassy appearance of cassava and potato starch films obtained by extrusion and blowing. These authors stressed that the starch humidity susceptibility and the plasticizer migration to the material surface caused blown bubble failures, as well as problems related to the film's stickiness. According to Thunwall *et al.* 

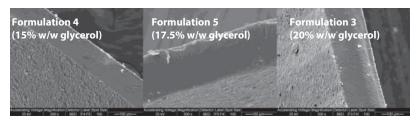


Figure 6.22 Cross-section SEM micrographs of starch-based films obtained by blown extrusion.

[147], an alternative to get over this problem could be to dry the pellets prior to film blowing. On the other hand, Buehler *et al.* [168] proposed the use of other plasticizers, such as sorbitol and urea, as a complement or replacement of glycerol. The films that were obtained by the extrusion and blowing method were not homogeneous with respect to their thickness (76–129  $\mu$ m) since this property depends on the insufflated gas flux during the blowing step and it was very difficult to control.

In order to evaluate TPS films morphology they were examined visually and by scanning electron microscopy (SEM). Figure 6.22 shows the surfaces and microstructures of starch films corresponding to formulations 3, 4 and 5 which contained 20, 15 and 17.5% w/w glycerol, respectively. All starch formulations allowed the obtainment of films with surfaces that presented a certain roughness, and their resultant structures were homogeneous and compact. The similar microstructure of the developed films could be attributed to the chemical compatibility between native and acetylated starches due to the low acetylation degree of the modified starch employed (0.5-0.8%). Herrera-Brandelero et al. [157] stressed that when two polymers are mixed by extrusion, it is relevant to achieve a single phase and avoid the formation of clusters from the entangled polymer chains. In Figure 6.22 there is no evidence of the presence of clusters, indicating that an adequate blend processing occurred. Besides, even though the TPS formulations contained different glycerol concentrations, this variation did not affect the appearance and homogeneity of the films' structures.

The TPS films were characterized determining their mechanical and barrier properties and the obtained results are shown in Table 6.14.

The WVP values of TPS films varied between 0.88 and  $1.41 \times 10^{-10}$  g/s m Pa. These results were lower than those reported by Flores *et al.* [28] for TPS cassava starch films  $(3.72-6.40 \times 10^{-10} \text{ g/s m Pa})$  obtained under similar operating conditions. Native starch and glycerol concentrations exerted a positive effect on this property, the plasticizer one being the most important due to its hydrophilic character. Cerqueira *et al.* [145] stressed that

Table 6.14 Properties of films based on native and acetylated corn starches plasticized with glycerol, obtained by blown extrusion technique.

Formulation <sup>1</sup>	AS/NS <sup>2</sup>	Mechanica	Mechanical properties	$WVP \times 10^{10}$		Gas permeability	<b>v</b>
		Tensile	Elongation at	(g/s m Pa)	$CO_3 \times 10^9$	$0_{3} \times 10^{10}$	Selective
		strength (MPa)	break (%)		(cm <sup>3</sup> /m̃ s Pa)	(cm <sup>3</sup> /m s Pa)	$P_{CO2}/P_{O2}$
1 (10:70:20)	0.14	$27.09 \pm 2.75^{a_3}$	$27.09 \pm 2.75^{a_3}  4.73 \pm 0.13^{a}$	$1.41 \pm 0.30^{a}$	$5.04\pm0.35^{\mathrm{a}}$	$4.13 \pm 0.11^{a}$	12.20
2 (80:5:15)	16	$16.25 \pm 0.42^{\rm b} \qquad 2.59 \pm 0.49^{\rm b}$	$2.59\pm0.49^{\mathrm{b}}$	$0.88 \pm 0.05^{b}$	$2.66\pm0.18^{\mathrm{b}}$	$2.08\pm0.08^{\mathrm{b}}$	12.78
3 (75:5:20)	15	$10.31 \pm 0.09^{\circ}$	$10.31 \pm 0.09^{\circ}$ $20.14 \pm 1.56^{\circ}$ $1.31 \pm 0.25^{a}$	$1.31 \pm 0.25^{a}$	$4.13 \pm 0.14^{\circ}$	$3.31 \pm 0.08^{\circ}$	12.47
4 (15:70:15)	0.21	$23.99 \pm 2.95^{a}$	$6.14 \pm 0.19^{d}$	$1.20 \pm 0.20^{a}$	$3.85\pm0.04^{\mathrm{d}}$	$2.98 \pm 0.08^{d}$	12.93
5 (45:37.5:17.5)	1.2	$17.54 \pm 1.92^{b}$ $3.92 \pm 0.25^{e}$		$1.36 \pm 0.17^{a}$	$4.62 \pm 0.12^{a}$	$3.65 \pm 0.22^{\circ}$	12.65
$^{1}$ (% w/w acetylated starch:% w/w matrixe starch:% w/w matrixe starch ratio: $^{3}$ Reported values correspond to the mean $\pm$ stan-	starch:% w/w na	tive starch:% w/w	glvcerol): <sup>2</sup> Acetvlat	ed to native starch	ratio: <sup>3</sup> Reported v	alues correspond t	o the mean + sta

Ś.  $\sqrt{2}$  when acceptance statistics with matter statistics with gravitation of the significant differences (p < 0.05).

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the action of this plasticizer on hydrocolloids films, especially on chitosan ones, increased the free volume and chain movements reducing the rigidity and increasing the molecular mobility, allowing higher water vapor transport through their structure. Acetylated starch incorporation into film formulations decreased their WVP due to the hydrophobic character of the substituent [15,29,74]. Films with the lowest WVP were those with low glycerol concentration and high acetylated/native ratio.

The TPS films presented the same behavior for oxygen and carbon dioxide ( $O_2$  and  $CO_2$ ) formulations; the highest glycerol concentration and the lowest acetylated/native ratio showed the highest gaseous permeability values. These results indicate that even though an increase in glycerol content enhanced films' mechanical properties, the obtained material presented higher gaseous permeabilities. A similar trend on films based on TPS was also reported by several authors [169,170]. Besides, starch films obtained from extrusion and blowing methods were selective with respect to gaseous permeabilities. The  $CO_2$  permeability values were significantly (p < 0.05) higher than those corresponding to  $O_2$  permeability; the selective coefficients are presented in Table 6.14. Development of biodegradable films with selective gaseous permeabilities could be very promising for controlling respiratory exchange and improving the conservation of fresh or minimally processed vegetables or foods susceptible to oxidation [146].

Table 6.14 also presented maximum tensile strength, as well as elongation at break values of TPS films. Obtained results evidenced that the strongest materials were those with a low acetvlated/native ratio, regardless of the glycerol concentration. Acetylated starch incorporation reinforced film matrix, increasing the maximum tensile strength. A similar trend was observed for starch-based films prepared by casting method [15]. Besides, obtained values of tensile strength for the developed films were higher than those reported by Zullo and Iannace [171] for blown films from different starch sources. Concerning elongation at break, it was observed that film flexibility was improved by increasing glycerol concentration. This trend was clearly evidenced by comparing the flexibility of the films corresponding to the formulations 2 and 3, since their ratios AS/NS were similar (16 and 15, respectively; Table 6.13). Films obtained from the formulation 3 with 20% glycerol presented flexibility 700% higher than those obtained from formulation 2 (15% plasticizer). However, for formulations with low AS/NS ratios (formulations 1 and 4, Table 6.14) this tendency was not observed; films with the highest glycerol concentration resulted in less flexibility.

## 6.5 Future Trends

The use of biodegradable packaging films by the food industry has become a topic of great interest, because of their potential for increasing the shelf life of many food products [172–175]. Biobased packaging has to supply a number of important functions in regard to the food product, including protection, maintenance of sensory quality and safety, and communication of information to the consumer [176].

Biopolymers, such as polysaccharides and proteins, are being studied as prospective replacements for synthetic polymers in the film and plastic industries. Their potential benefits are both environmental and cost related. Traditional techniques for processing thermoplastic synthetic polymers have been adapted to hydrophilic polymers such as starch.

The use of biodegradable films obtained from hydrocolloids for food packaging has been strongly limited mainly because of their poor water vapor barrier properties and weak mechanical properties. For this reason, natural polymers are frequently blended with other synthetic polymers or, less frequently, chemically modified with the aim of extending their applications [177,178].

Starch and its derivates are promising raw materials, due to their renewability from plants, industrial availability, and relative low cost [179,180]. It is known to be completely biodegradable in soil and water. As a packaging material, starch alone does not form films with appropriate mechanical properties unless it is first plasticized, or chemically modified. When starch is treated in an extruder by application of both thermal and mechanical energy, it can be converted to a thermoplastic material. In the production of thermoplastic starches, plasticizers are expected to efficiently reduce intramolecular hydrogen bonds and to provide stability to product properties. Research about the development of films based on TPS is promoted since starch can be processed employing the same technology used for synthetic polymers like extrusion, blowing, thermocompression or injection molding [42,181,182]. This advantage allows the use of actual machinery, making its processability easier and lowering industrial sector inversion. Unfortunately, TPS materials exhibit some disadvantages such as their strong hydrophilic character and poor mechanical and barrier properties compared to synthetic polymers [3,42]. An approach to overcome this limitation is to strengthen TPS matrixes with organic or mineral fillers [183]. These fillers reinforce biopolymeric matrixes and led to the development of films with special properties due to the synergic effect between the components. TPS composite films have a potential use as packaging materials for

food, cosmetics, and pharmaceutical products, among others. Lagaron and López-Rubio [183] have stressed the advantages of nanoclays inclusion in the formulation of active packaging based on bioplastics, which increase packaged food quality and safety.

Further studies should continue optimizing film formulation, as well as processing conditions, to improve humidity susceptibility and film properties for specific applications.

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# References

- 1. Averous, L., Boquillon, N. Biocomposites based on plasticized starch: Thermal and mechanical behaviours. *Carbohydr Polym* 56 (2):111–122, 2004.
- Gáspár, M., Benkõ, Zs., Dogossy, G., Réczey, K. Czigány, T. Reducing water absorption in compostable starch-based plastics. *Polym Degr Stab* 90 (3):563–569, 2005.
- Hernández-Izquierdo, V. M., Krochta, J. M. Thermoplastic processing of proteins for film formation: A review. J Food Sci 73 (2):30–39, 2008.
- Siracusa, V., Rocculi, P., Romani, S., Rosa, M. D. Biodegradable polymers for food packaging: A review. *Trends Food Sci Technol* 19 (12):634–639, 2008.
- 5. González-Gutierrez, J., Partal, P., García-Morales, M., Gallegos, C. Development of highly-transparent protein/starch-based bioplastics. *Bioresource Technol* 101:2007–2013, 2010.
- Álvarez-Chávez, C. R., Edwards, S., Moure-Eraso, R., Geiser, K. Sustainability of bio-based plastics: General comparative analysis and recommendations for improvement. *J Clean Prod* 23:47–56, 2012.
- Mali, S., Karam, L., Pereira, Ramos L., Grossmann, M. V. E. Relationships among the composition and physicochemical properties of starches with the characteristics of their films. *J Agric Food Chem* 52:7720–7725, 2004.
- Tapia Blácido, D., Sobral, P., Menegalli, F. Development and characterization of biofilms based on amaranth flour (Amaranthus caudatus). *J Food Eng* 67:215–223, 2005.
- 9. Bourtoom, T. Edible protein films: Properties enhancement. *Int Food Res J* 16:1–9, 2009.

#### 198 FUNCTIONAL POLYMERS IN FOOD SCIENCE

- García, M. A., Pinotti, A., Martino, M., Zaritzky, N. Characterization of starch and composite edible films and coatings. In *Edible Films and Coatings for Food Applications*, eds. M. Embuscado, and K. Huber, p. 169–209. New York: Springer, 2009.
- Piermaría, J., Bosch, A., Pinotti, A., Yantorno, O., García M. A., Abraham A. Kefiran films plasticized with sugars and polyols: Water vapor barrier and mechanical properties in relation to their microstructure analyzed by ATR/ FT-IR spectroscopy. *Food Hydrocolloid* 25:1261–1269, 2011.
- Tomé, L. C., Fernandes, S. C. M., Sadocco, P., Causio, J., Silvestre, A. J. D., Neto, C. P., Freire, C. S. R. Antibacterial thermoplastic starch-chitosan based materials prepared by melt-mixing. *BioRes* 7 (3):3398–3409, 2012.
- López, O. V., Giannuzzi, L., Zaritzky, N. E., García, M. A. Potassium sorbate controlled release from corn starch films. *Mater Sci Eng C* 33:1583–1591, 2013.
- 14. Xu, Y., Kim, K., Hanna, M., Nag, D. Chitosan-starch composite film: Preparation and characterization. *Ind Crops Prod* 21:185–192, 2005.
- 15. López, O. V., García, M. A., Zaritzky, N. E. Film forming capacity of chemically modified corn starches. *Carbohydr Polym* 73:573–581, 2008.
- Bello-Pérez, L. A., Agama-Acevedo, E., Sayago-Ayerdi, S. G., Moreno-Damian, E., Figueroa, J. D. C. some structural, physicochemical and functional studies of banana starches isolated from two varieties growing in Guerrero, México. *Starch/Stärke* 52:68–73, 2000.
- French, D. Organization of starch granules. In *Starch: Chemistry and Technology*, eds. R. L. Whistler, J. N. BeMiller, J. F. Paschall, pp. 183–247, Florida, USA: Academic Press Orlando, 1984.
- Mali, S., Grossmann, M. V. E., García, M. A., Martino, M., Zaritzky, N. Microstructural characterization of yam starch films. *Carbohydr Polym* 50:379–386, 2002.
- 19. Tharanathan, R. Biodegradable films and composite coatings: past, present and future: Critical review. *Food Sci Technol* 14:71–78, 2003.
- García, N., Famá, L., Dufresne, A., Aranguren, M., Goyanes, S. A comparison between the physico-chemical properties of tuber and cereal starches. *Food Res Int* 42:976–982, 2009.
- López, O. V., García, M. A. Starch films from a novel (Pachyrhizus ahipa) and conventional sources: Development and characterization. *Mater Sci Eng C* 32 (7):1931–1940, 2012.
- Alves, L. A., Vitolo, M., Felipe, M. G., Silva, J. B. Xylose reductase and xylitol dehydrogenase activities of Candida guilliermondii as a function of different treatments of sugarcane bagasse hemicellulosic hydrolysate employing experimental design. *Appl Biochem Biotechnol* 98:403–413, 2002.
- Romero-Bastida, C. A., Bello-Pérez, L. A., García, M. A., Martino, M., Solorza-Feria, J., Zaritzky, N. Physicochemical and microstructural characterization of films prepared by thermal and cold gelatinization from nonconventional sources of starches. *Carbohydr Polym* 60 (2):235–244, 2005.

- 24. Karam, L., Ferrero, C., Martino, M. N., Zaritzky, N. E., Grossmann, M. V. E. Thermal, microstructural and textural characterisation of gelatinised corn, cassava and yam starch blends. *Int J Food Sci Technol* 41 (7):805–812, 2006.
- 25. Zhang, Y., Han, J. Mechanical and thermal characteristics of pea starch films plasticized with monosaccharides and polyols. *J Food Sci* 71:109–118, 2006.
- Bertuzzi, M. A., Castro Vidaurre, E. F., Armada, M., Gottifredi, J. C. Water vapor permeability of edible starch based films. *J Food Eng* 80 (3):972–978, 2007.
- Famá, L., Goyanes, S., Gerschenson, L. Influence of storage time at room temperature on the physicochemical properties of cassava starch films. *Carbohydr Polym* 70:265–273, 2007.
- Flores, S. K., Costa, D., Yamashita, F., Gerschenson, L. N., Grossmann, M. V. E. Mixture design for evaluation of potassium sorbate and xanthan gum effect on properties of tapioca starch films obtained by extrusion. *Mater Sci Eng C* 30 (1):196–202, 2010.
- López, O. V., Viña, S. Z., Pachas, N. A., Sisterna, M. N., Rohatsch, P. H., Mugridge, A., Fassola, A. H., García, M. A. Composition and food properties of Pachyrhizus ahipa roots and starch. *Int J Food Sci Technol* 45:223–233, 2010.
- Shogren, R., Fanta, G., Doane, W. Development of starch based plastics: A reexamination of selected polymer systems in historical prospective. *Starch/ Stärke* 45 (8):276–280, 1993.
- Lafargue, D., Lourdin, D., Doublier, J. L. Film-forming properties of a modified starch/k-carrageenan mixture in relation to its rheological behavior. *Carbohydr Polym* 70 (1):101–111, 2007.
- 32. Fringant, C., Rinaudo, M., Foray, M. F., Bardet, M. Preparation of mixed esters of starch or use of an external plasticizer: Two different ways to change the properties of starch acetate films. *Carbohydr Polym* 35 (1–2):97–106, 1998.
- Tarvainen, M., Sutinen, R., Peltonen, S., Tiihonen, P., Paronen, P. Starch acetate: A novel film-forming polymer for pharmaceutical coatings. *J Pharm Sci* 91:282–289, 2002.
- Tarvainen, M., Peltonen, S., Mikkonen, H., Elovaara, M., Tuunainen, M., Paronen, RP. Aqueous starch acetate dispersion as a novel coating material for controlled release products. *J Control Release* 96:179–191, 2004.
- Bonacucina, G., Di Martino, P., Piombetti, M., Colombo, A., Roversi, F., Palmieri, G. F. Effect of plasticizers on properties of pregelatinised starch acetate (Amprac 01) free films. *Int J Pharm* 3 (13):72–77, 2006.
- Arvanitoyannis, I., Nakayama, A., Aiba S. Edible films made from hydroxypropyl starch and gelatine and plasticized by polyols and water. *Carbohydr Polym* 36:105–119, 1998.
- Fang, J. M., Fowler, P. A., Escrig, C., Gonzalez, R., Costa, J. A., Chamudis, L. Development of biodegradable laminate films derived from naturally occurring *Carbohydr Polym* 60 (1):39–42, 2005.

- 200 FUNCTIONAL POLYMERS IN FOOD SCIENCE
  - Gontard, N., Guilbert, S., Cuq, B. Edible Wheat gluten films: Influence of the main process variables on film properties using response surface methodology. J Food Sci 57 (1):190–199, 1992.
  - 39. Krochta, J. M., De Mulder-Johnston, C. Edible and biodegradable polymer films: Challenges and opportunities. *Food Technol* 51:61–74, 1997.
  - Neto, C. G. T., Giacometti, J. A., Job, A. E., Ferreira, F. C., Fonseca, J. L. C., Pereira, M. R. Thermal analysis of chitosan based networks. *Carbohydr Polym* 62 (2):97–103, 2005.
  - Vanin, F. M., Sobral, P. J. A., Menegalli, F. C., Carvalho, R. A., Habitante, A. M. Effects of plasticizers and their concentrations on thermal and functional properties of gelatin-based films. *Food Hydrocolloid* 19 (5):899–907, 2005.
  - Castillo, L., López, O., López, C., Zaritzky, N., García, M. A., Barbosa, S. E., Villar, M. A. Thermoplastic starch films reinforced with talc nanoparticles. *Carbohydr Polym* 95 (2):664–674, 2013.
  - Pérez, E. E., Mahfoud, A., Domínguez, C. L., Guzmán, R. Roots, tubers, grains and bananas; flours and starches: Utilization in the development of foods for conventional, celiac and phenylketonuric consumers. *J Food Process Technol* 4 (3):211, 2013. doi: 10.4172/2157-7110.1000211.
  - Donhowe, I. G., Fennema, O. R. Edible films and coatings: Characteristics, formation, definitions and testing methods. In *Edible Coatings and Films to Improve Food Quality*, eds. J. M. Krochta, E. A. Baldwin, M. Nisperos-Carriedo, pp. 1–21. Lancaster Pa: Technomic Pub Co, 1994.
  - 45. Gontard, N., Duchez, C., Cuq, J. L., Guilbert S. Edible composite films of wheat gluten and lipids: Water vapour permeability and other physical properties. *Int J Food Sci Technol* 19:39–50, 1994.
  - 46. Banker, G. S. Film coating theory and practice. *J Pharm Sci* 55 (1):81–89, 1986.
  - Gennadios, A., Weller, C. L., Hanna, M. A. Modification of physical and barrier properties of edible wheat gluten-based films. *Cereal Chem* 70 (4):426– 429, 1993.
  - Arvanitoyannis, I., Psomiadou, E., Nakayama, A., Aiba, S., Yamamoto, N. Edible film made from gelatin, soluble starch and polyols: Part 3. *Food Chem* 60 (4):593–604, 1997.
  - 49. Cuq, B., Gontard, N., Cuq, J. L., Guilbert, S. Selected functional of fish myofibrillar protein-based films as affected by hydrophilic plasticizer. *J Agric Food Chem* 45 (3):622–626, 1997.
  - Sothornvit, R., Krochta, J. Plasticizers in edible films and coatings. In Innovations in Food Packagings, ed. J. H. Han, pp. 403–428. Amsterdam, Netherlands: Elsevier, 2005.
  - 51. García, M. A., Martino, M. N., Zaritzky, N. E. Microstructural characterization of plasticized starch-based film. *Starch/Stärke* 52:118–124, 2000.
  - Han, J. H., Gennadios, A. Edible films and coatings: A review. In *Innovations in Food Packagings*, ed. J. H. Han, pp. 239–259. Amsterdam, Netherlands: Elsevier, 2005.

- 53. Forsyth, J. L., Ring, S. G., Noel, T. R. Characterization of starch from tubers of yam bean (Pachyrhizus ahipa). *J Agric Food Chem* 50:361–367, 2002.
- García, M. A., Martino, M. N., Zaritzky, N. E. Composite starch-based coatings applied to strawberries (Fragaria ananassa). *Nahrung/Food* 45 (4):267– 272, 2001.
- Rodriguez-Gonzalez, F. J., Ramsay, B. A., Favis, B. D. Rheological and thermal properties of thermoplastic starch with high glycerol content. *Carbohydr Polym* 58:139–147, 2004.
- 56. Bader, H. G., Göritz, D. Investigation on high amylose corn starch films. *Starch/Stärke* 46 (6):229–232, 1994.
- Shen, X. L., Wu, J. M., Chen, Y., Zhao, G. Antimicrobial and physical properties of sweet potato starch films incorporated with potassium sorbate or chitosan. *Food Hydrocolloid* 24 (4):285–290, 2010.
- Piermaria, J., Pinotti, A., García, M. A., Abraham, A. G. Films based on kefiran, an exopolysaccharide obtained from kefir grains: Development and characterization. *Food Hydrocolloid* 23:684–690, 2009.
- 59. Spiess, W., Wolf, W. The results of the COST 90 project on water activity. In *Physical Properties of Foods*, ed. R. Jowitt. London, UK: Applied Science Publisher, 1983.
- 60. Chang, Y. P., Cheah, P. B., Seow, C. C. Plasticizing-antiplasticizing effects of water on physical properties of tapioca starch films in the glassy state. *J Food Sci* 65:445–451, 2000.
- Coupland, J. N., Shaw, N. B., Monahan, F. J., O'Riordan, D., O'Sullivan, M. Modeling the effect of glycerol on the moisture sorption behavior of whey protein edible films. *J Food Eng* 43 (1):25–30, 2000.
- 62. Müller, C. M., Laurindo, J. B., Yamashita, F. Effect of cellulose fibers addition on the mechanical properties and water vapor barrier of starch-based films. *Food Hydrocolloid* 23:1328–1333, 2009.
- 63. Demirgöz, D., Elvira, C., Mano, J. Chemical modification of starch based biodegradable polymeric blends: effects on water uptake, degradation behaviour and mechanical properties. *Polym Degr Stab* 70:161–170, 2000.
- Guerra-Della Valle, D., Bello-Pérez, L. A., González-Soto, R. A., Solorza-Feria, J., Árambula-Villa, G. Effect of reaction time on the acetylation of plantain starch. *Revista Mexicana de Ingeniería Química* 7 (3):283–291, 2008.
- 65. Snyder, R. L., Bish, D. L. Quantitative analysis. In *Mineralogical Society* of *America Reviews in Mineralogy*, eds. D. L. Bish, J. E. Post, pp. 101–144. United States: Mineralogical Society of America, 1989.
- 66. Köksel, H., Sahbaz, F., Ozboy, O. The influence of wheat drying temperatures on the birefringence and X-ray diffraction patterns of wet harvested wheat starch. *Cereal Chem* 70 (4):481–483, 1993.
- 67. Van Soest, J. J., Hulleman, S. H., de Wit, D., Vliegenthart, J. F. Changes in the mechanical properties of thermoplastic potato starch in relation with changes in B-type crystalllinity. *Carbohydr Polym* 29 (3):225–232, 1996.

#### 202 FUNCTIONAL POLYMERS IN FOOD SCIENCE

- Van Soest, J. J., Esser, P. Influence of amylose/amylopectin ratio on properties of extruded starch plastic sheets. *J Macromol Sci: Part A* 34 (9):1665–1689, 1997.
- Klug, H. P., Alexander, L. E. X-Ray Diffraction Procedures: For Polycrystalline and Amorphous Materials. 2nd ed., eds. H. P. Klug, L. E. Alexander, pp. 992. New York: John Wiley & Sons, Inc., 1974.
- Roos, Y. H. *Phase Transitions in Foods*. San Diego, CA, USA, Academic Press, Inc., 1995.
- Even, W. R., Carr, S. H. Micromechanical fracture analysis of amylose. *Polymer* 19 (5):583–588, 1978.
- 72. Chang, B. S., Randall C. S. Use of subambient thermal analysis to optimize protein lyophilization. *Cryobiol* 29 (5):632–656, 1992.
- Guilbert, S., Gontard, N. Edible and biodegradable food packaging. In *Foods and Packaging Materials–Chemical Interactions*, eds. P. Ackermann, M. Jägerstad, T. Ohlsson, pp. 159–168. Cambridge: R. Soc. Chem., 1995.
- López, O., Lecot, C., Zaritzky, N., García, M. A. Biodegradable packages development from starch based heat sealable films. *J Food Eng* 105 (2):254– 263, 2011.
- Pommet, M., Redl, A., Guilbert, S., Morel, M. H. Intrinsic influence of various plasticizers on functional properties and reactivity of wheat gluten thermoplastic materials. *J Cereal Sci* 42 (1):81–91, 2005.
- Sobral, P. J. A., Menegalli, F. C., Hubinguer, M. D., Roques, M. A. Mechanical, water vapour barrier and thermal properties of gelatin based edible films. *Food Hydrocolloid* 15:423–432, 2001.
- 77. Iijima, M., Nakamura, K., Hatakeyama, T., Hatakeyama, H. Phase transition of pectin with sorbed water. *Carbohydr Polym* 41 (1):101–106, 2000.
- Psomiadou, E., Arvanitoyannis, I., Yamamoto, N. Edible films made from natural resources; Microcrystalline cellulose (MCC), methylcellulose (MC) and corn starch and polyols: Part 2. *Carbohydr Polym* 31:194–204, 1996.
- Myllarinen, P., Partanen, R., Seppala, J., Forssell, P. Effect of glycerol on behavior of amylose and amylopectin films. *Carbohydr Polym* 50:355–361, 2002.
- Da Roz, A., Carvalho, A., Gandini, A., Curvelo, A. The effects of plasticizers on thermoplastic starch compositions obtained by melt processing. *Carbohydr Polym* 63:417–424, 2006.
- Jiang, W., Qiao, X., Sun, K. Mechanical and thermal properties of thermoplastic acetylated starch/poly (ethylene-co-vinyl alcohol) blends. *Carbohydr Polym* 65:139–143, 2006.
- Forsell, P., Mikkilä, J., Moates, G., Parker, R. Phases and glass transition behaviour of concentrated barley starch-glicero-water mixtures, a model for thermoplastic starch. *Carbohydr Polym* 34:275–282, 1997.
- Ma, X., Chang, P., Yu, J., Stumborg M. Properties of biodegradable citric acidmodified granular starch/thermoplastic pea starch composites. *Carbohydr Polym* 75:1–8, 2009.

- 84. Hongsprabhas, P., Israkarn, K. New insights on the characteristics of starch network. *Food Res Int* 41:998–1006, 2008.
- Famá, L., Flores, S., Gerschenson, L., Goyanes, S. Physical characterization of cassava starch biofilms with special reference to dynamic mechanical properties at low temperatures. *Carbohydr Polym* 66:8–15, 2006.
- 86. Wilhelm, H., Sierakowski, M., Souza, G., Wypych, F. Starch films reinforced with mineral clay. *Carbohydr Polym* 52:101–110, 2003.
- 87. Cherian, G., Gennadios, A., Weller, C., Chinachoti, P. Thermo-mechanical behavior of wheat gluten films: effect of sucrose, glycerin, and sorbitol. *Cereal Chem* 72:1–6, 1995.
- Biliaderis, C., Lazaridou, A., Arvanitoyannis, I. Glass transition and physical properties of polyol-plasticised pullulan-starch blends at low moisture. *Carbohydr Polym* 40:29–47, 1999.
- 89. Mathew, A., Dufresne, A. Plasticized waxy maize starch: Effect of polyols and relative humidity on material properties. *Biomacromol* 3:1101–1108, 2002.
- Forssell, P., Hulleman, S. H., Myllärinen, P. J., Moates, G. K., Parker, R. Ageing of rubbery thermoplastic barley and oat starches. *Carbohydr Polym* 39:43–51, 1999.
- 91. Standard test methods for water vapor transmission of material, ASTM method ASTM. E96-95, Annual Book of ASTM Standards, Philadelphia, PA, 1995.
- 92. Galdeano, M. C., Mali, S., Grossmann, M. V. E., Yamashita, F., García, M. A. Effects of plasticizers on the properties of oat starch films. *Mater Sci Eng C* 29 (2):532–538, 2008.
- McHugh, T. H., Krochta, J. M. Milk-protein-based edible films and coatings. *Food Technol* 48:97–103, 1994.
- 94. McHugh, T. H., Krochta, J. M. Sorbitol- vs glycerol- plastyicized whey protein edible films: Integrated oxygen permeability and tensile properties evaluation. *J Agric Food Chem* 42:841–845, 1994.
- Miles, M. J., Morris, V. J., Ring, S. G. Gelation of amylose. *Carbohydr Res* 135 (2):257–269, 1985.
- Miles, M. J., Morris, V. J., Orford, P. D., Ring, S. G. The roles of amylose and amylopectine in the gelation and retrogradation of starch. *Carbohydr Res* 135 (2):271–281, 1985.
- 97. Noel, T. R., Ring, S. G. A study of the heat capacity of starch-water mixtures. *Carbohydr Res* 227:203–213, 1992.
- Baldwin, E. A., Nisperos-Carriedo, M. O., Hagenmaier, R. D., Baker, R. A. Use of lipids in edible coatings for food products. *Food Technol* 51:56–62, 1997.
- Hernandez, E. Edible coatings for lipids and resins. In *Edible Coatings and Films to Improve Food Quality*, eds. J. M. Krochta, E. A. Baldwin, M. Nisperos-Carriedo, p. 279–304. Lancaster Pa: Technomic Pub Co, 1994.
- 100. Betancur-Ancona, D., Chel-Guerrero, L., Camelo-Maros, R. I., Davila-Ortiz, G. Physicochemical and functional characterization of baby lima bean (Phaseolus lunatus) starch. *Starch/Stärke* 53 (5):219–226, 2001.

#### 204 FUNCTIONAL POLYMERS IN FOOD SCIENCE

- 101. Piyachomkwan, K., Chotineeranat, S., Kijkhunasatian, C., Tonwitowat, R., Prammanee, S., Oates, C. G., Sriroth, K. Edible canna (Canna edulis) as a complementary starch source to cassava for the starch industry. *Ind Crops Prod* 16:11–21, 2002.
- 102. Leonel, M., Sarmento, S. B., Cereda, M. P., Camara, F. L. Extração e caracterização de amido de jacatupe (Pachyrhizus ahipa). *Ciencia e Tecnologia Alimentaria Campinas* 23:362–365, 2003.
- 103. Noman, A. S. M., Hoque, M. A., Haque, M. M., Pervin, F., Karim, M. R. Nutritional and anti nutritional components in Pachyrhizus erosus L. *Tuber. Food Chem* 102:1112–1118, 2007.
- Famá, L., Rojas, A. M., Goyanes, S., Gerschenson, L. Mechanical properties of tapioca-starch edible films containing sorbates. *LWT-Food Sci Technol* 38 (6):631–639, 2005.
- Gennadios, A., Weller, C. L., Gooding, C. H. On the measurement of water vapor transmission rate of hydrophilic edible films. *J Food Eng* 21:395–409, 1994.
- 106. Garci'a, M. A., Martino, M. N., Zaritzky, N. E. Edible starch films and coatings characterization: Scanning electron microscopy, water vapor, and gas permeabilities. *Scanning* 21 (5):348–353, 1999.
- 107. García, M. A., Pinotti, A., Martino, M. N., Zaritzky, N. E. Characterization of composite hydrocolloid films. *Carbohydr Polym* 56:339–345, 2004.
- Parris, N., Coffin, D. R., Joubran, R. F., Pessen, H. Composition factors affecting the water vapor permeability and tensil properties of hydrophilic films. *J Agric Food Chem* 43:1432–1435, 1995.
- Parra, D. F., Tadini, C. C., Ponce, P., Lugao, A. B. Mechanical properties and water vapor transmission in some blends of cassava starch edible films. *Carbohydr Polym* 58:475–481, 2004.
- 110. Smith, S. A. Polyethylene, low density. In *The Wiley Encyclopedia of Packaging Technology*, ed. M. Bakker, pp. 514–523. New York: John Wiley & Sons, 1986.
- Garcia, M. A., Martino, M. N., Zaritzky, N. E. Lipid addition to improve barrier properties of edible starch-based films and coatings. *J Food Sci* 65:941– 944, 2000.
- 112. Arvanitoyannis, I., Kalichevsky, M., Blanshard, J. M., Psomiadou, E. Study of diffusion and permeation of gases in undrawn and uniaxially drawn films made from potato and rice starch conditioned at different relative humidities. *Carbohydr Polym 24*:1–15, 1994.
- 113. Cuq, B., Gontard, N., Guilbert, S. Proteins as agricultural polymers for packaging production. *Cereal Chem* 75 (1):1–9, 1998.
- Garcia, M. A., Martino, M., Zaritzky, N. E. Starch-based coatings: effect on refrigerated strawberry (Fragaria ananassa) quality. *J Sci Food Agric* 76 (3):411–420, 1998.
- Garcia, M. A., Martino, M. N., Zaritzky, N. E. Plasticized starch based coatings to improve strawberry (Fragaria Ananassa) quality and stability. *J Agric Food Chem* 46:3758–3767, 1998.

- 116. Cuq, B., Gontard, N., Guilbert, S. Edible films and coatings as active layers. In *Active Food Packaging*, ed. M. Rooney, pp. 111–142. Scotland: Blackie & Son Ltd, publishers, 1995.
- 117. Donhowe, I. G., Fennema, O. The effects of solution composition and drying temperature on crystallinity, permeability and mechanical properties of methylcellulose films. *J Food Process Pres* 17:231–246, 1993.
- 118. Standard Test Methods for Tensile Properties of Thin Plastic Sheeting, ASTM method ASTM, D882-91, Annual Book of ASTM, Philadelphia, PA, 1996.
- 119. Sarantópoulos, C., de Oliveira, L., Padula, M., Coltro, L., Alves, R., Correa García, E. Embalangens pláticas flexíveis, Principais polímeros e avaliação de propriedades Campinas: CETEA/ITAL, 2002.
- 120. Mali, S., Sakanaka, L. S., Yamashita, F., Grossmann, M. V. E. Water sorption and mechanical properties of cassava starch films and their relation to plasticizing effect. *Carbohydr Polym* 60:283–289, 2005.
- 121. García, M. A., Pinotti, A., Zaritzky, N. E. Physicochemical, water vapor barrier and mechanical properties of corn starch and chitosan composite films. *Starch/Stärke* 58 (9):453–463, 2006.
- 122. Laohakunjit, N., Noomhorm, A. Effect of plasticizers on mechanical and barrier properties of rice starch film. *Starch/Stärke* 56:348–356, 2004.
- 123. Shellhammer, T. H., Krochta, J. M. Edible films and barriers. In *Lipids-Industrial Applications and Technology*, eds. F. D. Gunstone, F. B. Padley. New York: Marcel Dekker, Inc., 1997.
- 124. Huang, C. Physicochemical, pasting and thermal properties of tuber starches as modified by guar gum and locust bean gum. *Int J Food Sci Technol* 44:50–57, 2009.
- 125. Rindlav-Westling, A., Stading, M., Gatenholm, P. Crystallinity and morphology in films of starch, amylose and amylopectin blends. *Biomacromol* 3 (1):84–91, 2002.
- 126. Zobel, H. F. Starch crystal transformations and their industrial importance. *Starch/Stärke* 40:1–7, 1988.
- 127. Cunningham, P., Ogale, A. A., Dawson, P. L., Acton, J. C. Tensile properties of soy protein isolate films produced by a thermal compaction technique. *J Food Sci* 65 (4):668–671, 2000.
- 128. Cho, S., Ullsten, H., Gällstedt, M., Hedenqvist, M. Heat-sealing properties of compression-molded wheat gluten films. *J Biobased Mater Bio* 1:56–63, 2007.
- 129. Brody, A., Marsh, K. *Wiley Encyclopedia of Packaging Technology*, 2nd ed., *eds*. A. Brody, K. Marsh. New York: John Wiley & Sons, 1997.
- 130. Standard Test Method for Seal Strength of Flexible Barrier Materials, ASTM method ASTM F88-00, Annual Book of ASTM Standards, Philadelphia, PA, 2001.
- 131. Osborn, K., Jenkins, W. *Plastic Films: Technology and Packaging Applications*. Pennsylvania. USA: Technomic Publishing Co., Inc., 1992.
- 132. Lacroix, M. Mechanical and permeability properties of edible films and coatings for food and pharmaceutical applications. In *Edible Films and Coatings*

*for Food Applications*, eds. M. E. Embuscado, K. C. Huber, pp. 347–366. New York, USA: Springer, 2009.

- 133. Possart, W., Deckhoff, S. Adhesion mechanism in a cyanurate prepolymer on silicon and on aluminium. *Int J Adhes Adhes* 19:425–434, 1999.
- Türe, H., Gällstedt, M., Hedenqvist, M. Antimicrobial compression-moulded wheat gluten films containing potassium sorbate. *Food Res Int* 45:109–115, 2012.
- 135. Pranoto, Y., Rakshi, S., Salokhe, V. Antimicrobial compression-moulded wheat gluten films containing potassium sorbate. *LWT Food Sci Technol* 38:859–865, 2005.
- 136. Quattara, B., Simard, R., Piette, G., Begin, A., Holley R. Diffusion of acetic and propionic acids from chitosan-based antimicrobial packaging films. J Food Sci 65:768–773, 2000.
- 137. Cagri, A., Ustunol, Z., Ryser, E. Antimicrobial edible films and coatings. *J Food Sci* 66:865–870, 2001.
- Li, Y., Liu, B., Zhao, Z., Bai, F., Chin, J. Optimized culture medium and fermentation conditions for lipid production by Rhodosporidium toruloides. *Biotechnol* 22:650–656, 2006.
- Chollet, E., Sebti, I., Martial-Gros, A., Degraeve, P. Nisin preliminary study as a potential preservative for ripened cheese: NaCl, fat and enzymes influence on nisin concentration and its antimicrobial activity. *Food Control* 19:982–989, 2008.
- 140. Flores, S., Famá, L., Rojas, A., Goyanes, S., Gerschenson, L. Physical properties of tapioca-starch edible films: Influence of filmmaking and potassium sorbate. *Food Res Int* 40:257–265, 2007.
- 141. Gliemmo, M., Campos, C., Gerschenson, L. Effect of sweet humectants on stability and antimicrobial activity of sorbates. *J Food Sci* 69:39–44, 2004.
- 142. Fajardo, P., Martins, J., Fuciños, C., Pastrana, L., Teixeira, J., Vicente, A. Evaluation of a chitosan-based edible film as carrier of natamycin to improve the storability of Saloio cheese. *J Food Eng* 101:349–356, 2010.
- 143. Stanojevic, D., Comic, L., Stefanovic, O., Solujic-Sukdolak, S. Antimicrobial effects of sodium benzoate, sodium nitrite and potassium sorbate and their synergistic action in vitro. *Bulg J Agric Sci* 15:307–311, 2009.
- 144. Sofos, J. N., Busta, F. F. Sorbic acid and sorbates. In *Antimicrobials in Foods*, eds. A. N. Branen, P. M. Davidson, pp. 49–94. New York: Dekker, 1983.
- 145. Cerqueira, M. A., Souza, B., Texeira, J, Vicente, A. Effect of glycerol and corn oil on physicochemical properties of polysaccharide ?lms: A comparative study. *Food Hydrocolloid* 27:175–184, 2012.
- 146. García, M. A., Pinotti, A., Martino, M., Zaritzky, N. Composite edible films and coatings. In *Edible Films and Coatings for Food Applications*, eds. M. Embuscado, K. Huber, pp. 169-210. India: Publisher Springer Science, 2009.
- Thunwall, M., Boldizar, A., Rigdhal, M. Compression molding and tensile properties of thermoplastic potato starch materials. *Biomacromol* 7:981–986, 2006.

- Thunwall, M., Kuthanová, V., Boldizar, A., Rigdahl, M. Film blowing of thermoplastic starch. *Carbohydr Polym* 71:583–590, 2008.
- 149. Pellissari, F., Yamashita, F., García, M. A., Martino, M., Zaritzky, N., Grossmann, M. V. E. Constrained mixture design applied to the development of cassava starch-chitosan blown films. *J Food Eng* 108:262–267, 2012.
- 150. Chen, B., Evans, J. R. G. Thermoplastic starch-clay nanocomposites and their characteristics. *Carbohydr Polym* 61:455–463, 2005.
- 151. Curvelo, A. A., Carvalho, A. J., Agnelli, J. A. Thermoplastic starch-cellulosic fibers composites: preliminary results. *Carbohydr Polym* 45:183–188, 2001.
- 152. Ma, X., Yu, J., He, K., Wang, N. The effects of different plasticizers on the properties of thermoplastic starch as solid polymer electrolytes. *Macromol Mat Eng* 292:503–510, 2007.
- 153. Ma, X., Chang, P., Yu, J., Stumborg, M. Properties of biodegradable citric acid-modified granular starch/thermoplastic pea starch composites. *Carbohydr Polym* 75:1–8, 2009.
- 154. Teixeira, E. M., Da Róz, A. L., Carvalho, A. J. F., Curvelo, A. A. S. The effect of glycerol/sugar/water and sugar/water mixtures on the plasticization of thermoplastic cassava starch. *Carbohydr Polym* 69:619–624, 2007.
- 155. Bastioli, C. Global status production of biobased packaging. *Starch/Stärke* 53:351–355, 2001.
- 156. De Graaf, A. R., Karman, A. P., Janssen, L, P. Material properties and glass transition temperature of different thermoplastic starches after extrusion process. *Starch/Stärke* 55:80–86, 2003.
- 157. Herrera-Brandelero, R., Grossmann, M. V. E., Yamashita, F. Effect of the method of production of the blends on mechanical and structural properties of biodegradable starch films produced by blown extrusion. *Carbohydr Polym* 86:1344–1350, 2011.
- Zhai, J., Chen, H., Colla, E., Wu, T. B. Direct current field adjustable ferroelectric behaviour in (Pb, Nb)(Zr, Sn, Ti)O3 antiferroelectric thin films. J Phys Condens Matter 15:963–969, 2003.
- 159. Shamekin, S., Myllärihen, P., Poutanen, K., Biosell, P. Film formation properties of potato starch hydrolysates. *Starch/Stärke* 54:20–24, 2002.
- Shogren, R. L., Fanta, G. F., Doane, W. M. Development of starch based plastics: A reexamination of selected polymer systems in historical perspective. *Starch/Stärke* 45:276–280, 1993.
- 161. Sala, R., Tomka, I. Water uptake in partially frozen and plasticized starch. In *The Glassy State in Foods*, eds. J. M. V. Blanshard, P. J. Lillford, pp. 483-489, United Kingdom: Nottingham University Press, 1993.
- 162. Vigneshwaran, N., Nachane, R. P., Balasubramanya, R. H., Varadarajan, P. V. A novel one-pot 'green' synthesis of stable silver nanoparticles using soluble starch. *Carbohydr Res* 341 (12):2012–2018, 2006.
- López, O. V., Zaritzky, N., Grossmann, M. V. E., García, M. A. Acetylated and native corn starch blend films produced by blown extrusion. *J Food Eng* 116:286–297, 2013.

#### 208 FUNCTIONAL POLYMERS IN FOOD SCIENCE

- 164. Srinivasa, P., Ramesh, M., Tharanathan, R. Effect of plasticizers and fatty acids on mechanical and permeability characteristics of chitosan films. *Food Hydrocolloid* 21:1113–1122, 2007.
- 165. Galicia-García, T., Martínez-Bustos, F., Jiménez-Arevalo, O., Martínez, A., Ibarra- Gómez, R., Gaytán-Martínez, M., Mendoza-Duarte, M. Thermal and microstructural characterization of biodegradable films prepared by extrusion and calendering process. *Carbohydr Polym* 83:354–361, 2011.
- Avérous, L., Fringant, C., Moro, L. Plasticized starch-cellulose interactions in polysaccharide composites. *Polym* 42:6565–6578, 2001.
- Móscicki, L., Mitrus, M., Wójtowicz, A., Oniszczuck, T., Rejak, A., Janssen, L. Application of extrusion-cooking for processing of thermoplastic starch (TPS). *Food Res Int* 47:291–299, 2011.
- 168. Buelher, F. S., Schmid, E., Schulz, H. J. U. S. Patent 5,346,936, 1994.
- 169. Rhim, J. Physical and mechanical properties of water resistant sodium alginate films. *LWT – Food Sci Technol* 37:323–330, 2004.
- 170. Stepto, R. Understanding the processing of thermoplastic starch. *Macromol Symp* 24:571–577, 2006.
- 171. Zullo, R., Iannace, S. The effects of different starch sources and plasticizers on film blowing of thermoplastic starch: Correlation among process, elongational properties and macromolecular structure. *Carbohydr Polym* 77:376–383, 2009.
- 172. Ahvenainen, R. Novel Food Packaging Techniques. Boca Raton, FL: CRC Press LLC, 2003.
- 173. Coles, R., McDowell, D., Kirwan, M. J. *Food Packaging Technology*. Oxford, UK: Blackwell Publishing Ltd, 2003.
- 174. Giles, G. A., Bain, D. A. Technology of plastics packaging for the consumer market. Boca Raton, FL: CRC Press LLC, 2001.
- 175. Hernandez, R., Selke, S. E. M., Cultler, J. *Plastics Packaging: Properties, Processing, Applications, Regulations.* Munich, Germany: Hanser Gardner Publications, 2000.
- 176. Robertson, G. L. *Food Packaging. Principles and Practice*. New York, NY: Marcel Dekker, 1993.
- 177. Guilbert, S., Cuq, B., Gontard, N. Recent innovations in edible and/or biodegradable packaging materials. *Food Addit Contam* 14:741–751, 1997.
- 178. Petersen, K., Nielsen, P. V., Bertelsen, G., Lawther, M., Olsen, M. B., Nilssonk, N. H. Potential of biobased materials for food packaging. *Trends in Food Sci Technol* 10:52–68, 1999.
- 179. Gonera, A., Cornillon, P. Gelatinization of starch/gum/sugar systems studied by using DSC, NMR, and CSLM. *Starch/Stärke* 54:508–516, 2002.
- Smits, A. L. M., Ruhnau, F. C., Vliegenthart, J. F. G. Ageing of starch based systems as observed with FT-IR and solid state NMR spectroscopy. *Starch/ Stärke* 50:478–483, 1998.

- Parra, D., Tadini, C., Ponce, P., Lugão, A. Mechanical properties and water vapor transmission in some blends of cassava starch edible films. *Carbohydr Polym* 58:475–481, 2004.
- Cyras, V. P., Manfredi, Ton-That, M. T., Vazquez, A. Physical and mechanical properties of thermoplastic starch/montmorillonite nanocomposite films. *Carbohydr Polym* 73:55–63, 2008.
- 183. Lagaron, J., López-Rubio, A. Nanotechnology for bioplastics: Opportunities, challenges and strategies. *Trends Food Sci Technol* 22:611–617, 2011.

# Polysaccharides as Valuable Materials in Food Packaging

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#### Abstract

The food industry is a large consumer of packaging materials. The main purpose of packaging is to protect the product from the surroundings and to maintain the safety and quality of packaged food. In addition, packaging must address communication, legal, and commercial demands. Other requirements for packaging materials include processability, heat sealability, recyclability or compostability, and low cost. Petroleum synthetic plastics show useful and convenient attributes and are therefore widely used as food packaging. However, a significant drawback is their permanence in the environment after use. The use of polymers derived from renewable resources, directly extracted/removed from natural materials, produced by classical chemical synthesis or produced by microorganisms or genetically transformed bacteria, could be an interesting alternative. In this sense, the potential use of polysaccharides alone or in combination with other substances as valuable materials in food packaging has been studied by several food companies and researchers during the last few years. Polysaccharide films and coatings have been used to extend the shelf life of fruits, vegetables, seafood, meats, and confectionary products by preventing dehydration, oxidation rancidity, surface browning, and oil diffusion; and, in some specific cases, they have been used to improve the physicochemical, nutritional, and sensorial properties of the products. The common polysaccharides used in food packaging are chitosan, cellulose, starches and their derivatives.

This chapter analyses the film-forming ability of polysaccharides and the physicochemical properties of this type of films, focusing on the way to obtain biodegradable films and the relationship between the structure and properties. Other

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aspects related to the production of polysaccharide-based films or packages, such as the effect of the addition of other components and applications of polysaccharide films have also been described.

*Keywords:* Polysaccharides, film formation, physicochemical properties, hydrocolloids, nanomaterials, food packaging

# 7.1 Introduction

The materials used for food packaging today consist of a variety of plastics, glass, metals, paper and cardboard, or combinations of materials of different chemical nature and physical structure. These materials, alone or used in various combinations, must provide physical protection and create proper physicochemical conditions for products that are essential for obtaining a satisfactory shelf life and maintaining food quality and safety.

Among the basic packaging materials, petroleum-based plastics have been widely used since the middle of the twentieth century. These materials have numerous advantages, including large scale availability and relatively low production cost. They are also lightweight and have excellent, versatile physicochemical properties [1]. However, after their useful life, they cause a serious environmental problem since they are not easily biodegraded [2,3]. In order to solve the problems generated by plastic waste, a great deal of research has been focused on the possible substitution of petro-based plastics by biodegradable materials with similar properties. Biopolymers derived from renewable biological resources are considered as potential substitutes for traditional non-biodegradable plastic films owing to their low cost, easy availability from reproducible resources and biodegradability [4]. Based on their origin and their manufacturing processes, the biopolymers can be broadly divided into three main categories: natural polymers extracted from marine and agricultural animals and plants such as polysaccharides and proteins, synthetic biodegradable polymers such as poly(l-lactide) (PLA), poly(glycolic acid) (PGA), poly(ε-caprolactone) (PCL), poly(butylene succinate) (PBS) or poly(vinyl alcohol) (PVA) and polymers produced directly by microbial fermentation such as microbial polyesters (poly(hydroxyalkanoates: PHAs, poly(β-hydroxybutyrate: PHB or poly(3-hydroxybutyrate-co-3-hydroxyvalerate: PHBV), or microbial polysaccharides: pullulan and curdlan [5].

In this context, edible films based on natural polymers appear as potential substitutes of synthetic packaging, thus playing a decisive role in the improvement of the shelf life of food through controlling gas transfer and being carriers of functional compounds. Edible films can be used as wrapping materials, stand-alone films, or can be fabricated into pouches and bags for subsequent packaging use. The main advantage of edible films over traditional synthetics is that they can be consumed with the products, but if the films are not consumed they contribute to the reduction of environmental pollution.

Several studies have reported the use of polysaccharides from different sources to prepare edible films with different properties, and have indicated that these carbohydrates are promising materials [6–8]. However, polysaccharide-based films are relatively stiff, and have a strong hydrophilic character compared with synthetic packaging films [9]. For this reason, research needs to focus on processing strategies to improve their poor properties. Some strategies are based on blends with lipids [10–12], synthetic polymers [13,14] or other biodegradable polymers with different properties [15]. The use of plasticizers [16] is another widely used strategy. Polysaccharides can easily be modified to improve their physicochemical properties by salt addition, solvent changes, heat gelatinization, pH changes, chemical modification of hydroxyl groups, crosslinking of polysaccharides, hydrolysis of polysaccharides, and applications of nanotechnology [17].

This chapter analyses the film-forming ability of polysaccharides and the physicochemical properties of these types of films, focusing on the way to obtain biodegradable films and the relationship between the structure and properties. Other aspects related to the production of polysaccharidebased films or packages, such as the effect of the addition of other components and applications of polysaccharides, have also been described.

# 7.2 Polysaccharides Used in Biodegradable Food Packaging

Common polysaccharides used in biodegradable food packaging are starch, cellulose, pectin, alginate, carrageenan and chitosan. These polymers are commonly extracted from natural resources such as plants and algae. An alternative to these polysaccharides are gums. Different varieties of exudate gums (gum arabic, mesquite gum), seed gums (locust bean gum and guar gum) and microbial fermentation gums (kefiran, pullulan, gellan and xanthan gum) are used for edible films and coatings.

#### 7.2.1 Starch

Starch is one of the most abundant natural polysaccharides, principally derived from tubers or cereals. This is not a uniform material since starches contain two types of glucose polymers: a linear chain molecule, called amylose, and a branched polymer of glucose, amylopectin [18]. The content of amylose in starch varies from 0 to 100%, depending on the botanic origins, but the most common starches contain about 25 percent of amylose and 75 percent of amylopectin. Amylose is responsible for the film-forming capacity of starch [19]. High amylose starch, such as corn starch, is a good source for film formation. Starch-based films, in that they are odorless, tasteless, colorless, nontoxic, biologically absorbable, flexible, oxygen impermeable, oil resistant, heat sealable and water soluble.

#### 7.2.2 Cellulose and Cellulose Derivatives

Cellulose is the most abundantly occurring natural polymer on earth and is a cheap raw material. It is a polysaccharide composed of linear chains of  $\beta$  (1–4) glucosidic units with methyl, hydroxypropyl or carboxyl substituents. The degree of methyl, hydroxypropyl or carboxyl substitution affects the physical and chemical properties of the material. The number of substituted hydroxyl groups per monomeric units is known as the degree of substitution (DS). Four cellulose derivative forms are used for food packaging: Hydroxypropyl cellulose (HPC), hydroxypropyl methylcellulose (HPMC), carboxymethyl cellulose (CMC) or methyl cellulose (MC). The MC, HPC and HPMC nonionic cellulose ethers are commercially available in powder or granular form, and in varying molecular weights and DS. They are insoluble in hot water but are soluble in cold water and organic solvents. CMC, which is an anionic cellulose ether, is available in a variety of types based on particle size, DS, viscosity and hydration characteristics for different food applications. It is soluble in hot and cold water but insoluble in organic solvents.

All of them have good film-forming characteristics. MC, HPMC, HPC and CMC films are generally transparent, flexible, odorless, tasteless, water soluble and resistant to oil and fats [20]. MC is the most resistant to water and it presents the lowest hydrophilic character among cellulose derivatives [21]; however, the water vapor permeability of cellulose ether film is still relatively high.

### 7.2.3 Pectin

Pectin is a family of heterogeneous branched polysaccharides composed of  $\beta$ -1,4-linked D-galacturonic acid residues, wherein the uronic acid carboxyls are either fully (HMP, high methoxy pectin) or partially (LMP, low methoxy pectin) methyl-esterified. It is a food additive which is mainly used for its gelling and stabilizing abilities. Pectin films can control water activity, preventing moisture loss from food by acting as a sacrificial agent. It can potentially limit fat migration, provide a barrier to gas, and help to trap flavor and aroma, and carry and present antioxidants or antimicrobials. High-methoxyl pectin forms excellent films; low-methoxyl pectin forms gels in the presence of calcium ions and can also be used for developing edible films.

### 7.2.4 Alginate

Alginates, polysaccharides derived from seaweeds, are known as potential biopolymer films due to their unique and well-studied colloidal properties; these include thickening, stabilizing, suspending, film-forming, gelproducing and emulsion-stabilizing properties [22]. Edible films prepared from alginates form strong, uniform, transparent and water-soluble films. Due to their hydrophilic nature, alginates exhibit poor water resistance, but they have good oxygen barrier properties and can retard lipid oxidation in foods. Desirable properties attributed to alginate films include moisture retention, shrinkage reduction, improved product texture, juiciness, color, and aroma of foods. Alginates can also be put to versatile use in encapsulation [23]. The treatment of alginate films with divalent cation (calcium, magnesium, manganese, aluminum, or iron) solutions converts these into insoluble films.

#### 7.2.5 Carrageenan

Carrageenan is a water-soluble polymer with a linear chain of partially sulphated galactans, extracted from red seaweed (*Rhodophyceae*). It is widely used in the food industry to improve thickening and texture qualities and to stabilize food products. There are three main varieties of carrageenan, *lambda, iota* and, *kappa*, which differ in the number of sulphate groups, 41, 33 and 20% (w/w) respectively. While *kappa* and *iota* carrageenans form gels, *lambda* is unable to do so and is used as a pure thickener. In general, carrageenan forms uniform, transparent and water-soluble films with good mechanical properties and has been applied to a variety of foods to carry

antimicrobials and to reduce moisture loss, oxidation, or disintegration [24]. Carrageenan has also been studied for flavor encapsulation [25]. Of the three varieties, *kappa*-carregeenan exhibits the greatest tensile strength.

### 7.2.6 Chitosan

Chitosan is an edible and biodegradable polymer derived from chitin, the second most abundant natural and nontoxic polymer (after cellulose) and is found in the exoskeleton of crustaceans, in fungal cell walls and other biological materials. It is a copolymer consisting of  $\beta$ -(1-4)-2-acetamido- $\delta$ -glucose and  $\beta$ -(1-4)-2-amino- $\delta$ -glucose units with the latter usually exceeding 80%. Chitosans are described in terms of the degree of deacety-lation and average molecular weight; and, their importance resides in their antimicrobial properties in conjunction with their cationicity and their film-forming properties [26]. Chitosan forms films with excellent oxygen barrier properties, good mechanical properties and good antimicrobial activity. However, a major drawback of chitosan is its high water vapor permeability.

### 7.2.7 Exudate Gums

Exudate gums are structurally complex heteropolysaccharides obtained from natural exudates of different tree species. Gum arabic and mesquite gum are examples of exudate gums that can be used for edible films and coatings. Gum arabic, owing to its solubility in hot or cold water, is the least viscous of the hydrocolloid gums. It has been used as a protective film on oily foods to eliminate their moist, oily appearance and provide a low-calorie product. The mesquite gum forms films with excellent water vapor barrier properties when small amounts of lipids are added to their formulation [27].

### 7.2.8 Seed Gums

Examples of seed gums that can be used for edible films and coatings are locust bean gum and guar gum. Locust bean gum is a neutral polysaccharide consisting of  $\beta$ -D-mannopyranosyl and  $\alpha$ -D-galactopyranosyl units in a ratio of 4:1. Guar gum is a polysaccharide having a straight chain of  $\beta$ -D-mannopyranosyl with single  $\alpha$ -D-galactopyranosyl units attached as side chains in a ratio of 1:2. Both are soluble in water (locust bean gum must be heated to be dissolved) and are highly viscous. Locust bean gum

is generally used as a thickener or viscosity modifier, binder of free water, suspending agent or stabilizer in cheeses, frozen confections, bakery products, pie fillings, meats, sauces and salad dressings. Guar gum is used as a water binder and stabilizer and viscosity builder. It is used in dairy, bakery and meat products; as well as in beverages and salad dressings.

#### 7.2.9 Microbial Polysaccharides

Kefiran, pullulan, gellan and xanthan gum are examples of microbial polysaccharides that have been tested to produce biodegradable films [28-30]. Kefiran, an exopolysaccharide produced by microorganisms present in the kefir grains, is a glucogalactan that has several health-promoting properties. Kefiran improves the viscosity and viscoelastic properties of acid milk gels [31] and is also able to form gels with interesting viscoelastic properties itself at low temperatures [32]. Pullulan is a water soluble, random coil glucan gum, insoluble in organic solvents and non-hygroscopic in nature. Its aqueous solutions are stable and exhibit a relatively low viscosity as compared to other polysaccharides. Pulullan gum forms clear, odorless and tasteless films with good oxygen barriers. Generally, pullulan films are commonly combined with other polysaccharides or proteins to improve the functional properties of edible films. Gellan gum is a watersoluble polysaccharide, produced by the fermentation of a pure culture of Pseudomonas elodea. The gel of gellan gum can be formed by dispersing the gellan gum in water, heating, adding cations, and then cooling to set. The gel texture can be modified by blending with other gums, especially the gelling gums. Gellan gum forms transparent, stronger and more brittle films than alginate or carrageenan films. Xanthan gum is produced by fermentation from the organism Xanthomonas campestris. It is soluble in both cold and hot water and has a high degree of viscosity. Thanks to its thickening, suspending and stabilizing effects, it is used in salad dressings, dry mix products, icings and frostings, confectionery, dairy products, fruit gels, sauces, syrups and baked goods. It can be used to provide uniform coating, good clinging qualities, improved adhesion in wet batters, and to prevent moisture migration during frying [33].

### 7.3 Formation and Main Characteristics of Polysaccharide-Based Films

The development of films from water-soluble-gel-forming polysaccharides has brought a surge of new types of coatings for extending the shelf life of a wide variety of food products. Polysaccharide films are poor moisture barriers but, in contrast, they have moderately low oxygen permeability and, at the same time, selective permeability to this gas and  $CO_2$  [34]. A major goal for future research is to reduce the hydrophilic nature of polysaccharide coatings and films while maintaining the desirable gas permeability of this type of films. Polysaccharide polymers, such as cellulose, must first undergo hydrolysis or derivitization to become water soluble.

Cellulose is the most abundant polysaccharide in the world. MC, HPMC and HPC are nonionic water-soluble ethers with good film-forming properties. In order to avoid the formation of agglomerates, the dissolution of these nonionic cellulose ethers must be performed in two steps: dispersion and hydration. Wherever possible, they should be put into solution before other soluble ingredients are added or should be dispersed in a water miscible non-solvent, such as glycerol, ethanol or propylene glycol, and then this slurry added to water. The solutions of these cellulose ethers are stable at pH 2-11 and are compatible with surfactants, other water-soluble polysaccharides, and with salts. The procedure for the preparation of clear CMC solutions follows that of the nonionic cellulose ethers, except for the pH conditions. The CMC solutions are only stable at pH 7-9. CMC is compatible with a wide range of other food ingredients, including proteins, sugars, starches and other hydrocolloids.

Edible coatings, including MC, HPC, HPMC or CMC, have been applied to a variety of foods to provide moisture, oxygen or oil barriers, and to improve batter adhesion. These cellulose-ether films are generally transparent, flexible, odorless, tasteless, water soluble, and resistant to oils and fats [33,34]. The MC films do not have good moisture barrier, but provide an excellent barrier against the migration of fats and oils and can be used to reduce oil absorption in fried products. HPC is thermoplastic and capable of injection molding and extrusion. It can retard spoilage and moisture absorption in coated nuts and candies. The film-forming characteristics of HPMC upon heating provide an effective film that can reduce oil absorption in certain reformed products. CMC forms a complex in the presence of casein, increasing the coating's formulation viscosity. It retains the firmness of fruits and vegetables, preserves the important flavor components of some fresh commodities, reduces the oxygen uptake without causing an increase in carbon dioxide in fruits and vegetables, and improves the puncture strength of caseinate-based films [34].

Starch is one of the most naturally abundant polysaccharide raw materials. It is a renewable resource, inexpensive, and widely available. Edible or biodegradable starch films can be obtained from the native starch or its components, amylose and amylopectin, by means of two main techniques: solution casting and subsequent drying (wet method) and thermoplastic processing (dry method) [35]. Modified [36] and soluble or pre-gelatinized starch have also been used [37] to obtain starch films. For edible starch films, it is important to prepare a clear starch solution with proper solid concentration, in order to ensure both the continuity of films and the ease of casting. A solid concentration of 10-15% is suggested for casting conventional starch films [38]. At higher concentrations, the solution is too viscous to be cast; and at low concentrations, the solution of completely solubilized starch polymers has low-level gelling results, causing problems for the process of forming a continuous film of sufficient thickness [39]. The complete solubilization of starches in water requires high temperatures and can be facilitated using amylose-complexing agents, like butanol. Aqueous starch solutions are normally unstable, and in this sense, it is necessary to keep the starch solution at a temperature above their gelation temperature prior to casting. When the solid concentration is 10–15%, the gelation temperature is 60–74°C [40]. Generally, films produced from edible starches are odorless, tasteless, and colorless and exhibit physical characteristics, chemical resistance and mechanical properties similar to those of plastic films [41]. Otherwise, starch films may be obtained by using a dry process (thermoplastic or thermal processing) in which the water content is lower when compared to the wet process. A dry process can also be used with those raw materials which present thermoplastic properties; this means that they become soft (melted or rubbery) at a temperature lower than the decomposition temperature and so can be molded into a determined shape when submitted to a thermal/mechanical process. Although starch does not present this characteristic in its native state, it is capable of becoming a thermoplastic material if it is treated correctly.

Carrageenans are used mainly in gel formation, in stabilizing suspensions and emulsions, and for the gelation and structural viscosity of milk-based products. Carrageenan gels can also be used as food coatings. Carrageenan-based coatings have long been applied to a variety of foods to incorporate antimicrobials or antioxidants, and to reduce moisture loss, oxidation, or disintegration [34]. Choi *et al.* [42] reported that the t-carrageenan film containing potassium sorbate under study had great potential to form antimicrobial food packaging with valuable properties for extending the shelf life or increasing the safety of foods. The ı-carrageenanbased edible films have good mechanical characteristics and present low oxygen transfer. The addition of lipids to form emulsified films decreases water vapor transfer and could be used to encapsulate active molecules or aroma compounds [25,43]. Fabra *et al.* [44] reported that ı-carrageenan improves the tensile properties and water vapor permeability of sodium caseinate-oleic acid-beeswax films, though the barrier properties of lipidfree films decreased when ı-carrageenan was added.

Alginates possess good film-forming properties, which make them particularly useful in food applications. Divalent cations are used as gelling agents (to induce ionic interactions, followed by hydrogen bonding) in the formation of alginate films [21]. Films and coatings can be made from a sodium alginate solution; these films and coatings can be produced by means of a rapid reaction with a cold application of calcium, forming intermolecular associations involving the G-block regions [33]. The treatment of alginate films with divalent cations (i.e., calcium solutions) converts them into insoluble films [45]. Although alginate films are quite brittle, they may be further plasticized with glycerol [22,46-48]. Due to their highly hydrophilic nature, alginate-based films are poor moisture barriers; although alginate gel coatings can significantly reduce moisture loss from foods, because the moisture is lost from the coating before the food dehydrates [49]. Fabra et al. [44] evaluated the effect of adding alginates to sodium caseinate-lipid films. In lipid-free films, alginates improved their tensile properties, although the water vapor permeability values increased. However, in sodium caseinate-lipid films, the addition of alginates to protein matrices produced less flexible, less stretchable and more permeable films.

Regarding pectins, the characteristics of obtained films vary depending on the type of pectin. Generally, high-methoxyl pectin forms excellent films and low-methoxyl pectin, derived from controlling esterification, forms gels in the presence of calcium ions and can also be used for developing edible films. Despite their hydrophilic nature, pectinate coatings can control water activity, preventing moisture loss from food by acting as a sacrificial agent. It can potentially limit fat migration, provide a barrier to gas, help to trap flavor and aroma, and carry antioxidants or antimicrobials [50]. In addition, the incorporation of lipids may improve water vapor barrier properties. Plasticized blends of citrus pectin give strong, flexible films which are thermally stable up to 180°C [51].

Chitosan is of interest as a potential edible film component because of its excellent oxygen barrier properties [33,49,52,53] and its good mechanical properties. However, it is highly permeable to water vapor [54,55].

Inherent antibacterial properties and the film-forming ability of chitosan make it an ideal choice for use as a biodegradable antimicrobial packaging material that can be used to improve the storability of perishable foods. It has been confirmed that chitosan films exhibit good antimicrobial activity, which can help extend the food shelf life [56–61].

Agar forms transparent, strong and flexible films even at low moisture levels. Their water vapor permeability quality did not appreciably differ in comparison to starch films, arabinoxylan films or cellulose derivative films. Moreover, agar-based films were found to be heat sealable. Phan The *et al.* [62] demonstrated that agar can potentially provide a very good cohesive matrix, which contributes towards enhancing the tensile properties of other polysaccharide films, such as cassava starch or arabinoxylan.

Pullulan films cast from aqueous solutions are clear, odorless and tasteless and are good oxygen barriers [49,63]. Pullulan films are commonly combined with other polysaccharides (alginate, carboxymethylcellulose) or proteins (whey protein, sodium caseinate) to improve the functional properties of edible films [64–67]. Tong *et al.* [67] reported that by incorporating alginate and CMC into pullulan, the water barrier and mechanical properties were weakened significantly. On the other hand, the addition of low concentrations of pullulan to whey protein isolate films improved the functional properties of whey protein isolate-based films, modifying the oxygen and water vapor barrier properties of these films [65].

Gellan gum films are transparent, stronger and more brittle than alginate or carrageenan [46]. Gellan films can also be used as a carrier of antimicrobials or antioxidants [68].

# 7.4 Physicochemical Properties of Polysaccharide-Based Materials

Due to the hydrophilic nature of these polymers, polysaccharide-based films exhibit limited water vapor barrier ability. However, films based on polysaccharides, such as alginate, cellulose ethers, chitosan, carrageenan or pectins, exhibit good gas-barrier properties. Mechanical and barrier properties are generally related to the physical and chemical nature of the polymers. Generally, the properties of polysaccharide-based films are very sensitive to changes in relative humidity. At low relative humidity, these films tend to crack while, at high relative humidity, these films swell and their barrier characteristics are markedly degraded.

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Barrier properties are important to separate food components or foods from the environment, which causes food deterioration. At low to intermediate relative humidity levels, polysaccharide-based films and coatings are good barriers against oxygen and other nonpolar substances, such as aromas and oils, due to their highly packed and ordered hydrogen-bonded networked structure [69]. Nevertheless, due to their hydrophilic nature, they are indeed wettable by water and generally exhibit limited water vapor barrier ability, especially at high relative humidity levels. However, certain polysaccharides, applied in the form of high moisture gelatinous coatings, can retard moisture loss from coated foods by functioning as sacrificing agents rather than moisture barriers.

Tables 7.1 and 7.2 show the water vapor permeability and gas permeability values of different polysaccharide films. Comparisons have to be made with caution since the data come from different studies, where different test conditions (temperature and relative humidity) are used, which affect the obtained values. Polysaccharide films appear to have higher water vapor permeability and lower oxygen permeability values than synthetic polymers. Glycerol, which is commonly used as a plasticizer to form polysaccharide films, promotes the increase of water and oxygen permeability values as the plasticizer content increases. Of the polysaccharide films, the starch films have the best water barrier properties; both the starch and chitosan-based films have better oxygen barrier properties than HPMC films.

The mechanical properties reflect the durability of films and the ability of a coating to enhance the mechanical integrity of foods. Polysaccharide films are relatively stiff and, therefore, plasticizers are needed to facilitate their handling and to achieve the desirable plasticity.

Table 7.3 shows the tensile parameters (EM: Elastic Modulus, TS: Tensile strength at break, E: Elongation at break) of different polysaccharidebased films. Polysaccharide films appear to have similar tensile strength and lower elongation at break values than synthetic polymer films. HPMC, alginate, pectin and chitosan films have the highest TS values. The addition of some additives, such as montmorillonite (MMT), modified the barrier and mechanical properties of these polysaccharide-based films. For instance, starch-CMC films containing MMT had lower elongation at break and higher TS values.

The glass transition temperature (Tg) of the polymers, which are greatly affected by the polymer mean molecular weight and the water and plasticizer content, defines the temperature range from within which polysaccharide films exhibit adequate plastic deformation, without brittleness. Table 7.4 shows some values of Tg for different polymer films equilibrated at different water activity levels, containing plasticizers or not. Completely

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Composition (dry basis)	Test conditions	WVP $\cdot 10^{10}$ (g $\cdot m^{-1} \cdot s^{-1} \cdot Pa^{-1}$ )	Reference
HPMC	38°C; 0–90% RH	6.1 (0.9)	[70]
HPMC:gly 1:0.04		6.59 (0.03)	
Methylcellulose:gly 1:0.45	25°C; 0-100% RH	0.475 (0.014)	[71]
Chitosan	25°C; 53-100% RH	19 (3)	[72]
Chitosan:wheat starch <sup>1</sup> 50:50		16 (4)	
Wheat starch <sup>1</sup>		13 (2)	
Sodium alginate:gly 1:0.25	25°C; 30-100% RH	0.84 (0.07)	[73]
Pectin:gly 1:0.5		1.73 (0.08)	
HPMC:gly 1:0.25	25°C; 53–100% RH	23.1 (1.2)	[74]
HPMC:corn starch 50:50 <sup>2</sup>		23.6 (1.1)	
Corn starch:gly 1:0.25		21.9 (0.6)	
Chitosan + 75% plasticizers <sup>3</sup>	25°C; 50–100% RH	36 (2)	[75]
ı-carrageenan + 75% plasticizers <sup>3</sup>		19.0 (0.3)	
Agar:gly 1:0.15	25°C; 22–57% RH	0.72 (0.03)	[62]
Cassava starch:gly 1:0.15		0.56 (0.02)	
Agar:gly 1:0.15	25°C; 22–99% RH	1.37 (0.09)	
Cassava starch:gly 1:0.15		1.12 (0.07)	

 Table 7.1
 Water vapor permeability of polysaccharide films (vs synthetic films).

Composition (dry basis)	Test conditions	WVP $\cdot 10^{10}$ (g $\cdot m^{-1} \cdot s^{-1} \cdot Pa^{-1}$ )	Reference
Pullulan:gly 1:0.25	20°C; 0–100% RH	1.22	[67]
Sodium alginate:gly 1:0.25		2.69	
CMC:gly 1:0.25		3.61	
Alginate:gly 2:1.5	25°C; 33-100% RH	3.0 (0.1)	[76]
Alginate:gly:SO 2:1.5:0.025		2.9 (0.2)	
Gellan:gly 0.5:0.6		2.7 (0.1)	
Gellan:gly:SO 0.5:0.6:0.025		2.2 (0.2)	
Polyvinyl chloride (PVC)	28°C; 0–100% RH	0.0718	[77]
Polyethyleneterephthalate (PET)	25°C; 0–100% RH	0.0197	
LDPE	28°C; 0–100% RH	0.0036	
<sup>1</sup> Wheat starch contains 15% glycerol (w/w).			

<sup>2</sup>Glycerol content was 25% (d.b).

<sup>3</sup>Mixture of glycerol and PEG (50:50).

HPMC: hydroxypropylmethylcellulose. SO: sunflower oil.

Composition	Test conditions	$O_2$ permeability · 10 <sup>12</sup> (cm <sup>3</sup> ·m <sup>-1</sup> ·s <sup>-1</sup> ·Pa <sup>-1</sup> )	$CO_2$ permeability $\cdot 10^{12}$ ( $cm^3 \cdot m^{-1} \cdot s^{-1} \cdot Pa^{-1}$ )	Reference
MC	24°C; 54% RH	1.12		[78]
HPMC		3.15		
Quinoa starch + 21.2% glycerol	25°C; 58% RH	0.050 (0.012)		[29]
Chitosan	10°C; 58% RH	0.017 (0.005)		[72]
Chitosan	25°C; 58% RH	0.011 (0.002)		
HPMC:gly 1:0.25 (NPF)	25°C; 53% RH	2.85 (0.04)		[74]
HPMC:gly 1:0.25 (SF)		7.4 (0.9)		
Corn starch:gly 1:0.25 (NPF)		0.04(0.01)		
Corn starch:gly 1:0.25 (SF)		0.042 (0.004)		
MC:gly 9:1	30°C; 0% RH	2.2 (0.5)		[80]
HPC:gly 9:1		3.57 (0.03)		
MC:gly 9:1	21°C; 0% RH		69 (19)	
HPC:gly 9:1			144(4)	
Cellulose:corn starch:lignin 50:40:10	25°C; 0% RH	1.43 (0.07)	1.51(0.11)	[81]
Cellulose:corn starch:lignin 73:25:2		1.48 (0.12)	2.44 (0.13)	
Cellulose:corn starch:lignin 80:15:5		1.50 (0.11)	1.79 (0.1)	
Cellulose:corn starch:lignin 90:1:9		1.49 (0.06)	2.49 (0.09)	
Regenerated cellulose		1.27 (0.10)	1.52 (0.09)	

 Table 7.2 Gas barrier properties of polysaccharide films (vs synthetic films).

Composition	Test conditions	$O_2$ permeability · 10 <sup>12</sup> (cm <sup>3</sup> ·m <sup>-1</sup> ·s <sup>-1</sup> ·Pa <sup>-1</sup> )	$\begin{array}{ c c c c } CO_2 permeability \cdot 10^{12} & Reference \\ (cm^3 \cdot m^{-1} \cdot s^{-1} \cdot Pa^{-1}) \end{array}$	Reference
Polyester	23°C; 50% RH	0,181		[82]
LDPE		21,64		[83]
HDPE		4,942		
Ethylene Vinyl Alcohol (EVOH; 70% VOH)	23°C; 95% RH	0,139		[83]

MC: methylcellulose. HPMC: hydroxypropylmethylcellulose. NPF: newly prepared films. SF: 5 weeks stored films. HPC: hydroxypropylcellulose.

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Table 7.3 Mechanical properties of polysaccharide films (vs synthetic films) (EM: Elastic modulus, TS: Tensile strength, E: Elongation at break).

, ,					
Film composition	Films conditionedElastic modulusbefore and/orEM (MPa)	Elastic modulus EM (MPa)	Tensile strength TS (MPa)	Elongation E (%) Reference	Reference
	during tests				
HPMC	20°C; 50% RH	2490 (50)	65 (7)	4.3 (1.0)	[20]
Starch-CMC	21°C; 55% RH		(9.0) 8.6	63 (6)	[84]
Starch-CMC-1% MMT			13.1 (0.8)	44 (5)	
Starch-CMC-3% MMT			16.5 (1.3)	36.8 (1.1)	
Starch-CMC-5% MMT			21.9 (0.8)	24 (5)	
Starch-CMC-7% MMT			27.5 (1.1)	18 (3)	
Wheat starch <sup>1</sup> (NPF)	25°C; 53% RH	1356 (190)	33 (9)	3.5 (0.9)	[72]
Wheat starch <sup>1</sup> (SF)		1300 (170)	12 (5)	1.8 (0.7)	
Chitosan:wheat starch <sup>1</sup> 50:50 (NPF)		1590 (120)	46 (2)	5 (2)	
Chitosan:wheat starch <sup>1</sup> 50:50 (SF)		1600 (300)	45 (6)	5.6 (1.3)	
Alginate	25°C; 53% RH		35 (8)	9 (2)	[73]
Pectin			23 (2)	6 (1)	
Corn starch:gly 1:0.25 (NPF)	25°C; 53% RH	800 (70)	9.1 (0.6)	8 (4)	[74]
Corn starch:gly 1:0.25 (SF)		1470 (160)	20 (2)	2.2 (0.2)	
HPMC:gly 1:0.25 (NPF)		1300 (60)	25 (5)	10(4)	
HPMC:gly 1:0.25 (SF)		1040(40)	23 (4)	19 (2)	

Film composition	Films conditionedElastic modulusTensile strengthElongation E (%)Reference	Elastic modulus	Tensile strength	Elongation E (%)	Reference
	before and/or	EM (MPa)	TS (MPa)		
	during tests				
Cellulose:corn starch:lignin 85:10:5	Wet films <sup>2</sup>		16.2 (1.9)	92 (4)	[81]
Cellulose:corn starch:lignin 85:15:0			7 (1)	69 (4)	
Cellulose:corn starch:lignin 95:5:0			8.6 (1.0)	63 (3)	
Cellulose:corn starch:lignin 95:0:5			15.2	91 (3)	
Low-densitypolyethylene (LDPE)	25°C; 50% RH		9–17	500	[85]
High-densitypolyethylene (HDPE)			17–35	300	
Polypropylene(PP)			42	300	
Oriented polypropylene (OPP)			165	50-75	
<sup>1</sup> Wheat starch contains 15% glycerol (w/w).					

VIIEAL STALCH COLLEALIS 1.7% BLYCELOI (W/W).

<sup>2</sup>Films were measured immediately after immersed in water for 30 min.

HPMC: Hydroxypropylmethylcellulose. CMC: Carboxymethylcellulose. MMT: Montmorillonite. NPF: Newly prepared films. SF: 90 days or 5 weeks stored films (Bonilla et al., 2013 & Jiménez et al., 2012b respectively).

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Composition (dry basis)	Water activity (a <sub>w</sub> )	Tg (°C)	Reference
HPMC <sup>1</sup>	03	150.5 (1.6)	[70]
HPMC:gly <sup>1</sup> 1:0.04		145.7 (1.3)	
Starch:CMC <sup>2</sup>	0.55	162.1	[84]
Starch:CMC + 1% MMT <sup>2</sup>		169.7	
Cassava starch	0.58	131.9	[86]
Cassava starch:gly 1:0.15		97.9	
Cassava starch:gly 1:0.30		62.2/ -55.7	]
Cassava starch:gly 1:0.45		42.1/ -58.8	
Pectin	0	37	[87]
Corn starch:gly 1:0.25	0	50 (4)	[88]
	0.53	48.3 (3)	]
	0.68	10.3 (1.4)	
	0.75	1 (3)	
Chitosan	0.45	170	[89]
Gellan + glycerol <sup>3</sup>		-12.2	[90]
SSPS	0.53	31 (3)	[9]
SSPS:gly 1:0.2		24.7 (1.5)	
SSPS:gly 1:0.3		21.9 (1.5)	
SSPS:gly 1:0.4		20 (4)	
Pullulan	0.23	58.67	[91]
	0.43	51.03	
	0.65	41.51	
	0.84	38.89	
Sodium alginate	0.23	56.03	
	0.43	52.46	]
	0.65	39.96	]
	0.84	35.12	]

**Table 7.4** Glass transition temperature of polysaccharide-based films obtainedfrom DSC analysis.

<sup>1</sup>Measurements were carried out by using perforated pans.

<sup>2</sup>Films contain citric acid as cross-linking agent.

<sup>3</sup>Glycerol content was not specified.

CMC: carboxymethylcellulose. MMT: montmorillonite. SSPS: soluble soybean polysaccharide.

dried HPMC, both with and without glycerol, showed very high Tg values where the effect of glycerol at 4% provoked a drop of 5°C as compared to HPMC [70]. Starch:CMC blend films, containing citric acid as the crosslinking agent, equilibrated at 55% relative humidity, also showed very high values of Tg [84]; while a lower value was obtained for cassava starch, which was greatly reduced when growing amounts of glycerol (0 to 45% with respect to starch) were added to the films equilibrated at 58% relative humidity [86]. For corn starch, containing 25% glycerol with respect to starch, very similar values to cassava starch containing a similar amount of glycerol and with the same level of water activity were obtained [88]. The effect of glycerol was also observed in the case of soluble soy bean polysaccharide (SSPS) equilibrated at 53% relative humidity, although all the values were in the range of the room-handling temperature [9]. Pullulan and sodium alginate also showed relatively low Tg values, mainly when equilibrated at high relative humidity (84%) [91].

# 7.5 Functionalization of Polysaccharide Materials

To improve the properties of polysaccharide films in order to substitute conventional polymers (polyethylene, polyethylene terephthalate, etc.) and to obtain biodegradable packaging, different strategies have been tested. In this sense, different studies have been carried out in the last few years which have used different polysaccharides, such as alginate [76,92], cellulose derivatives [10,67,93] or starch [94,95]. Despite their potential as environmentally friendly materials, polysaccharides present some drawbacks that make their application difficult on an industrial scale, such as the fact that, as previously mentioned, most polysaccharides are highly hydrophilic and therefore very sensitive to moisture action. In addition, the mechanical properties of some polysaccharides, such as starch, are too deficient to be used as packaging. Furthermore, the gas barrier ability of other polysaccharides, such as HPMC, is very poor in comparison with starch or ethylene vinyl alcohol (EVOH) (Table 7.2).

The mechanical behavior of starch-based materials can be improved by the addition of plasticizers (usually polyols) that reduce the brittleness of the matrix, in relationship with the presence of attractive forces between starch chains [96]. Glycerol, sorbitol and other compounds have been added to the film-forming dispersions to decrease these attractive intermolecular forces [97–99]. In the previous chapter (6: Films Based on Starches), this information and other aspects related with starch-based packaging are extensively reviewed. It has been reported that lipids and other nonpolar compounds have been used to form composite films so as to increase the hydrophobicity of polysaccharide materials. In this way, fatty acids, paraffin, triolein or vegetable oils have been used in emulsified films [25,100,101]. Lipid addition allows us to obtain better water vapor barriers but other properties such as mechanical behavior or transparency may be negatively affected. Nowadays, the sensitivity of polysaccharides to moisture action, their barrier ability and other characteristics can be improved by the addition of other components which increase the functionality of these materials. In this sense, blends with different hydrocolloids and nanomaterials have been evaluated as a real alternative of obtaining highly functional biodegradable packaging.

#### 7.5.1 Blends with Other Hydrocolloids

Some properties of polysaccharide-based films can be improved by blending them with other polysaccharides or proteins. The combination of different polysaccharides allows us to obtain materials with improved properties, whereas the incorporation of proteins permits us to improve the hydrophobicity of the film, coherent with the protein's amphiphilic nature.

One of the most widely-studied polysaccharide blends is the starch-chitosan blend. These polymers form a homogeneous and continuous matrix, as has been observed in different studies [72,102,103]. Bonilla et al. [72] obtained films by using different ratios of starch and chitosan in order to improve the properties of starch. They found that the mechanical properties of blend films were significantly improved in comparison with pure starch films, since the mechanical resistance (tensile strength) and elongation at break increased after chitosan was added. These results were linked with a plasticizing effect of chitosan which favored the film extension and plastic deformation during tensile tests. On the contrary, the oxygen permeability and water vapor permeability increased when chitosan was added in comparison with pure starch films, although the differences were not significant. In addition, blend films showed a relevant antimicrobial activity when the starch:chitosan ratio was 50:50. These authors also studied the effect of storage time on the physical properties of starch:chitosan films and observed that chitosan was able to avoid starch retrogradation.

The inhibition of starch retrogradation by the addition of other hydrocolloids has also been observed by Jiménez *et al.* [74]. These authors obtained corn starch films with HPMC, which is an amorphous polymer [104]. The HPMC inhibited starch recrystallization, although it gave rise to a poorer oxygen barrier. These starch-HPMC blends exhibited phase separation, as the authors observed by means of scanning electron microscopy. The lack of miscibility between starch and HPMC gave rise to a starch-rich phase (on the bottom) and an HPMC rich-phase (on the top). The phase separation of polysaccharide blends has also been found in other polysaccharide blends [103,105].

One of the most commonly-used methods with which to improve the miscibility of components or to increase the interactions between polymer chains is the use of crosslinking agents such as ferulic acid [103], tannic acid [106] or citric acid [107]. Mathew and Abraham [103] found that starch-chitosan films were more homogeneous when ferulic acid was incorporated, which was explained by the crosslinking activity of this organic acid. The starch-chitosan film with ferulic acid was stronger and more stable and flexible than the film without the crosslinking agent. They used FTIR analysis to confirm the presence of interactions between the film components. The addition of ferulic acid led to the improvement in the water vapor and oxygen barrier properties and the mechanical resistance of the blend films, while the lipid peroxide inhibition capacity was also enhanced.

Another polysaccharide that has been used to improve the properties of starch films is agar. Wu *et al.* [81] obtained starch-agar films and evaluated their barrier ability and their mechanical behavior. They found that the addition of 5–15% agar yielded homogeneous films in which both polymers were compatible due to the presence of hydrogen bonds between polymer chains, in agreement with the FTIR results. Composite films were more resistant and flexible (higher tensile strength and elongation values) and less permeable in a high moisture environment.

In a more recent work, Rhim and Wang [108] obtained blend hydrogel films by using agar,  $\kappa$ -carrageenan and konjac glucomannan. These films, based on hydrogels, presented three-dimensional networks that swell by absorbing and retaining a large amount of water without dissolving or losing their integrity in water [109]. The properties of the ternary blend film were not improved to a great extent in comparison with the pure components. Nevertheless, the effect of the hydration, which is particularly problematic in single-biopolymer films, where water-polymer interactions compete effectively with polymer-polymer interactions [110], is mitigated in the ternary blend, which is useful for obtaining an antifogging film. As Farris *et al.* [110] explained, polymer-polymer interactions can be strengthened by combining biopolymers with different structures and introducing predominantly electrostatic interactions rather than hydrogen bonding. As previously mentioned, some features of polysaccharide films may be improved by the addition of proteins. In this sense, different studies, which evaluate the properties and functionality of polysaccharide-protein films, have been published in the last few years [111–113].

Wang *et al.* [114] studied films where sodium alginate, whey protein isolate (WPI) and gelatin were combined in different proportions to obtain films with improved functionality. They studied different properties, such as the mechanical behavior of films or their oxygen and water vapor barrier ability. In most cases, even though the smallest proportion was that of sodium alginate, the authors concluded that the properties of edible films were improved by combining proteins and polysaccharides.

The polysaccharide:protein ratio used in composite film formulation can be optimized, depending on the final use of the material. In this sense, Lee *et al.* [111] studied the mechanical properties of gellan/gelatin films and concluded that the change in the ratio of two polymers modifies the strength and extensibility of the films. The tensile strength increased linearly as the gellan content increased, whereas the tensile elongation decreased as the gellan content rose.

Another polysaccharide-protein composite that has been studied as a potential edible/biodegradable material for food applications is WPImesquite gum [113]. Regardless of the WPI:mesquite gum ratio, all the samples were homogeneous, which points out that both polymers were compatible and able to form film-forming solutions and films. Nevertheless, the roughness (the higher the proportion of mesquite gum, the rougher) obtained from atomic force microscopy observations indicated that the interactions between polymers were related with the WPI:mesquite gum ratio and the net charge of the polymers. In this sense, both polymers are negatively charged, thus favoring electrostatic repulsion and promoting the formation of aggregates. These authors observe that the incorporation of mesquite gum helped to obtain more flexible and extensible films coherent with an increase in the plastic deformation. Taking these observations into account, the authors conclude that the polysaccharide-protein blend may form films with adequate properties, avoiding the use of low molecular weight plasticizers.

Low and medium moisture polysaccharide packaging films are usually totally functional. Nevertheless, their properties are greatly affected under high moisture conditions since the internal structure is affected by polymer-water interactions. To solve this problem, which affects most polysaccharides and proteins, it is possible to form hydrogel films, as previously commented on [108]. One of the polysaccharides that may be used for food applications at high moisture contents is alginate. Recently, Harper *et al.* [115] studied the influence of gelatin, whey and soy protein on the properties of "wet" alginate films (moisture content up to 90%) used to obtain sausage casings. The addition of proteins reduced the puncture force in comparison with pure alginate film, thus indicating that these components led to weakened "wet" alginate films. The lower puncture force was observed for films containing heated WPI and unheated protein isolate, which concurs with light microscopy observations. In these images, protein clumps, which disrupt the internal structure, can be clearly observed. Of all the studied samples, it seems that alginate-gelatin is the best composite since the puncture force decreases but not to a significant extent. In addition, this blend had the lowest water loss of all the alginate-protein gels, implying that it may be the most compatible alginate-protein gel.

The fact that the addition of proteins led to an improvement in the properties of polysaccharide films is also observed by Jiménez *et al.* [116]. These authors obtained films based on corn starch and sodium caseinate in different ratios and studied their different physicochemical properties after different storage times. The incorporation of sodium caseinate to starch matrices reduced the crystallinity of starch films and inhibited starch retrogradation during film storage. Although blend films showed higher oxygen permeability, films prepared by using both hydrocolloids presented better potential applications than pure starch films, mainly due to the inhibition of starch crystallization which implies undesirable changes in the film mechanical behavior.

Jiménez *et al.* [117] also studied the effect of the incorporation of hydrophobic compounds (oleic acid and/or  $\alpha$ -tocopherol) into starch-sodium caseinate blend films (50:50 ratio) in order to reduce the water vapor permeability and to obtain antioxidant biodegradable films. The lipid incorporation provoked phase separation in starch-sodium caseinate films, due to the different interactions with each polymer (amphiphilic protein and hydrophilic starch). In addition, although lipids only slightly affected the water vapor barrier properties, depending on the film storage time, the incorporation of oleic acid greatly increased oxygen permeability. This effect was also expected for  $\alpha$ -tocopherol, but it was mitigated by the antioxidant activity of this compound, which conferred antioxidant capacity to the films. The obtained results pointed out that, in complex matrices in which more than one polymer are included, the interactions between components have to be considered carefully in order to predict the final behavior of the materials adequately.

#### 7.5.2 Addition of Nanomaterials

Nowadays, the incorporation of nanomaterials is one of the most promising strategies for improving the functionality of biodegradable polymers. These components can be divided into several groups depending on their origin and structure. In this sense, polysaccharides have been studied as matrices of nanocomposites by using nanoclays [118–120], cellulose nanoparticles [120,121], chitin nanoparticles [122], carbon nanotubes [123], silver nanoparticles [118] or nanoliposomes [124,125].

Layered silicate nanoclays, mainly montmorillonite, have been incorporated into biodegradable matrices so as to obtain materials with greater mechanical resistance and improved barrier properties. The increase in the mechanical resistance (higher tensile strength) has been found by authors in different polysaccharide matrices [119,120,126]. Rhim [119] explained that this effect is related not only with the very high elastic modulus of the clay and large surface area, but also with the stronger interfacial interaction through hydrogen or ionic bonds between the polysaccharide chains and intercalated layered silicate [84]. Abdollahi et al. [120] obtained alginate films with incorporated MMT nanoparticles. They found a linear decrease in water vapor permeability as the nanoclay content increased in the formulations. The authors related this effect with the tortuous path caused by layered silicate nanoparticles distributed homogeneously in the matrix. The reduction in water vapor permeability brought about by the addition of layered nanoclays has been reported in other polysaccharides, such as chitosan [118], agar [119] or starch [127]. As regards the water vapor uptake ratio, Rhim [119] found that adding nanoclays to agar matrices led to a reduction in this parameter, coherent with the strong interaction between polymer chains and clay nanoparticles.

Other nanomaterials that have been incorporated into polysaccharide films are cellulose nanoparticles. Bilbao-Sainz *et al.* [121] obtained HPMC-based films with different incorporated cellulose nanoparticles. These components were cellulose nanofibrils, oxidized cellulose nanofibrils and cellulose whiskers. The size of the particles ranged from  $301 \pm 67$ nm, in the case of cellulose whiskers, to  $35 \pm 9$  nm, corresponding to cellulose nanofibrils. The effect of adding the cellulose nanoparticles differed depending on the type of particle. Cellulose nanofibrils improved neither the mechanical performance nor the water vapor barrier of the HPMC films. On the contrary, cellulose nanowhiskers improved both properties. As far as the transparency of films is concerned, this parameter was reduced by between 35 and 42% when cellulose nanofibrils were added. When cellulose whiskers were incorporated into the films, the decrease in the transparency was very slight (6%) in comparison with the pure HPMC films.

Chang *et al.* [122] used chitin nanoparticles to improve the functionality of starch-based films. The incorporation of these particles led to films being obtained with higher tensile strength and glass transition temperature and lower water vapor permeability. On the contrary, the elongation of films decreased linearly as more nanoparticles were added. The improvement of the abovementioned properties is related with the good interfacial interaction between the nanoparticles and the starch matrices when chitin nanoparticles are added at low concentrations. At high levels, these particles tended to conglomerate, giving rise to microcomposites, as found by Rhim [119] while working with agar-nanoclay composites. Referring to nanoclays, Alexandre and Dubois [128] explained that when the polymer is unable to intercalate between the silicate sheets, a phase-separated composite is obtained, whose properties remain in the same range as traditional microcomposites.

The most widely used means of increasing the antimicrobial effect of biodegradable and conventional polymers is through the incorporation of silver nanoparticles. One of the main advantages of their addition is that they are wide-spectrum antimicrobials, as reported by Rhim *et al.* [118]. The addition of silver nanoparticles to chitosan-based films was able to inhibit the growth of both Gram + (*Staphylococcus aureus, Listeria mono-cytogenes*) and Gram- (*Salmonella typhimurium, Escherichia coli*) bacteria. Other studies have reported the antimicrobial activity of silver nanoparticles in agar [129] or alginate [130] matrices.

In general, nanoparticles or nanomaterials are ultrafine particles in the nanometer size range, which are able to form nanobiocomposite films when combined with natural polymers [131]. Recently, Zhang et al. [124] have produced lecithin nanoliposomes which have been incorporated into chitosan matrices, thus giving rise to nanocomposites. They used fish, rapeseed and soy lecithin and studied the physycochemical properties of the obtained films, mainly focusing their results on tissue engineering applications. Another study, carried out by Jiménez et al. [125], presented the application of rapeseed and soy lecithin nanoliposomes as carriers of antimicrobial compounds. In this piece of work, starch-sodium caseinate matrix was used and nanoliposomes containing orange essential oil and D-limonene were incorporated into the matrix. The incorporation of volatile antimicrobials into nanoliposomes avoided their loss by evaporation during film drying, although the mechanical resistance of the matrix (due to the introduction of discontinuities) and their transparency (due to the natural color of lecithins) were affected by their addition.

### 7.6 Applications of Polysaccharide-Based Materials in Food Packaging

Many studies have pointed out the benefits of the application of polysaccharide-based packaging to food products (Table 7.5). Polysaccharides may be used to form a coating on the surface of food products to increase their shelf life or to avoid mass or moisture transfer [132,133,136], to substitute conventional polymers by forming bags for food products [94,140] or to improve the performance of conventional polymers by means of the formation of multilayers [141,142].

Bravin *et al.* [10] obtained an edible coating based on corn starch, methylcellulose and soybean oil and studied its effectiveness at controlling moisture transfer in cereal crackers. In addition, they studied the effect of the thickness and the deposition process used for film-forming dispersions (spreading and spraying). The authors identified that an atomization pressure of 2 bar and a film thickness of 30  $\mu$ m were optimum for the application of an edible coating to bakery products. Furthermore, they found that a coating application increased the shelf life (in terms of crispness) of crackers at different relative humidities.

Polysaccharides have also been used to reduce oil consumption during the frying of food products. García *et al.* [132] obtained methylcellulose-sorbitol-based coatings to reduce the oil consumption in wheat flour discs and potato chips. Samples were immersed for 10 s in the coating solution and immediately fried. They found a decrease of up to 35% in the oil consumption during the frying of both products. In a more recent study, Singthong and Thonkaew [143] applied sodium alginate, carboxy-methylcellulose and pectin-based coatings to banana chips. The highest reductions in oil consumption corresponded with banana chips blanched in 0.5% CaCl<sub>2</sub> and coated with 1% pectin or 1% carboxymethylcellulose (w/w). In these cases, oil consumption was reduced from 40 g/100 g chips to 22.89 and 22.90 g/100 g chips, respectively.

The main application of polysaccharide-based materials is the increase in the shelf life of highly perishable products, such as fresh-cut fruit and vegetables and meat products. Maqbool *et al.* [135] applied an arabic gum:chitosan based coating (1:0.1) to fresh banana to prevent the growth of *Colletotrichum musae* (anthracnose). They found a reduction in the incidence of anthracnose in fresh fruits after 28 days at 13°C and 80% relative humidity and 5 days under marketing conditions (25%, 60% RH). The control of fungi growth was also studied by Perdones *et al.* [137]. They obtained chitosan-lemon essential oil-based coatings which were applied

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Table 7.5         Some applications of polysaccharide-based materials on food packaging and preservation.	saccharide-based mater	ials on food packaging	g and preservation.	
Polysaccharide matrix	Other compounds	Food product	Effect	Reference
Methylcellulose-starch + glycerol	Soybean oil	Cereal crackers	Increase of the shelf-life (in terms of crispness) at different relative humidity	[10]
Starch	Polyester	Fresh beef steaks	Biodegradable film was able to substitute PVC conventional packaging to preserve the quality of fresh beef steaks	[94]
Methylcellulose + sorbitol	1	Potato chips and wheat flour discs	Reduction of the oil consumption during frying	[132]
Chitosan Arabic gum	1	Carambola fruit	Polysaccharide coatings had a beneficial impact on the quality retention of carambola fruit dur- ing storage	[133]
Native and modified maize and cassava starch	-	Pumpkin slices	Significant decrease in the losses of carotene during hot air drying (70°C)	[134]
Arabic gum-chitosan		Banana	Reduction of the incidence of anthracnose in fresh fruits after 28 at 13°C and 80% RH and 5 days under marketing condi- tions (25%, 60% RH)	[135]

Polysaccharide matrix	Other compounds	Food product	Effect	Reference
Alginate	Enterocines	Cooked ham	Alginate films slowed down the growth of L. Monocytogenes after 8 days of storage at 6°C	[92]
Water chestnut starch-chitosan	Perilla oil	Mongolian cheese	Increase of the shelf-life in terms of microbial growth delay and weight loss	[95]
Tragacanth gum	Aloe vera gel	Button mushroom	Better preservation of mushrooms during 13 days of storage at 4, 10 and 15°C	[136]
НРМС	Beeswax	Plums	Coating of fresh fruits increased the self-life of the product under controlled storage conditions	[93]
Chitosan	Lemon essential oil	Strawberry	Better preservation of fruits due to fungal decay after storage during 7 days at 5°C	[137]
Chitosan	Olive and rosemary oleoresines	Pumpkin slices	Reduction of the polyphenol oxidase (PPO) and peroxidase (POD) activities	[138]
Alginate	Ascorbic acid	Fresh-cut mangoes	Edible coating contributed to maintain the colour and the antioxidant potential of fresh-cut fruits after storage during 12 days at 4°C	[139]

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to fresh strawberries. The antifungal effect of chitosan and essential oil contributed to a better preservation of fruits after 7 days' storage at 5°C.

In some cases, the reduction in quality is related with color changes, connected or not with the oxidation of components, or with the moisture loss of food products. Robles-Sánchez *et al.* [139] obtained alginate-ascorbic acid coatings which were applied to fresh-cut mangoes. This coating allowed the color and the antioxidant potential of fresh-cut fruits to be maintained after 12 days' storage at 4°C. Ponce *et al.* [138] applied chitosan coatings with incorporated oleoresines to pumpkin slices. In this case, the coating was able to reduce the polyphenol oxidase (PPO) and peroxidase (POD) activities, thus maintaining the natural color of the product. In a more recent study, Lago-Vanzela *et al.* [134] analyzed how starch-based coatings reduced the amount of carotene lost during the hot-air drying of pumpkin slices. The results showed that applying the coating before drying gave rise to dehydrated products with better color and a significantly higher retention of trans- $\alpha$ -carotene and trans- $\beta$ -carotene than the products without this pretreatment.

Polysaccharide materials may also be used as carriers of active compounds to prevent the spoilage of food products. In this way, Marcos *et al.* [92] carried out a study in which they obtained alginate coatings with incorporated enterocines. The authors used these coatings on the surface of cooked ham and found that alginate films slowed down the growth of *L. Monocytogenes* after 8 days' storage at 6°C.

As previously commented on, polysaccharides may be used to form packaging materials like conventional synthetic ones. Cannarsi *et al.* [94] studied the possibility of substituting conventional PVC film packaging for a starch-polyester biodegradable composite film. To this end, they prepared different beef steak samples, packaged by using the conventional PVC film and two biodegradable films: a composite film based on starch and biodegradable polyester and another composed of a mixture of three biodegradable polyesters. The samples were stored at 4 and 15°C to simulate the conventional storage conditions and thermal abuse, respectively. After 6 days' storage, the color of the samples as well as the total viable counts and spoilage microorganism counts were measured. The authors concluded that there were no significant differences between the conventional PVC film and those containing biodegradable polymers. Therefore, starch may be used to obtain flexible biodegradable films to substitute, in some applications, conventional petroleum-derived polymers.

Chitosan has also been used to obtain polysaccharide-based packaging. Schreiber *et al.* [140] obtained gallic acid-grafted chitosan to prevent the oxidation of packaged peanuts. These authors found that chitosan films grafted with gallic acid were able to reduce the oxidation of peanut powder after 15 weeks at 50°C under low humidity conditions, compared with low density polyethylene films. These results may be attributed to the presence of a primary antioxidant and to the low oxygen permeability of chitosan in comparison with LDPE (see Table 7.2).

The ability of some polysaccharides to avoid the oxygen transfer allows some conventional polymers to be substituted in multilayer systems. In this way, the biodegradability of the final material increases, whereas the cost and the consumption of synthetic polymers significantly decrease. Laufer et al. [142] obtained multilayered, thin films by using chitosan (CH), carrageenan (CR) and montmorillonite (MMT). Trilayer films (CH/MMT/ CR) were able to reduce the oxygen permeability of a PET film by an order of magnitude under dry conditions, whereas the presence of an additional layer of CH reduced the oxygen permeability by two orders of magnitude under the same conditions. To demonstrate the effectiveness of the multilayered films, these authors studied the browning of coated and noncoated samples, stored at room temperature and humidity (22°C and 55% RH). After 9 days' storage, uncoated samples were almost entirely brown, whereas coated bananas had just a few brown speckles. Thin films were obtained by using the layer-by-layer method, which is a powerful means of assembling gas barrier multilayer thin films by the sequential adsorption of oppositely charged polyelectrolites or particles [144]. This method has also been used by Gu et al. [141] to obtain multilayer-coated biaxially-oriented poly (lactic acid) films, by assembling alternating layers of sodium alginate (ALG)/polyethyleneimine (PEI). They studied the water vapor and oxygen barrier properties of films as well as their mechanical and optical properties to evaluate the possibility of competing with synthetic polymers (PE, PET) in food packaging applications. The water vapor permeability was significantly reduced (25%), while the studied films were highly transparent. The mechanical properties of PLA films improved slightly (higher tensile strength and elongation at break) as the number of layers increased. Nevertheless, the most relevant result was the very low oxygen permeability found for the 30-layer ALG/PEI coating  $(4.8 \cdot 10^{-8} \text{ cm}^2 \cdot \text{s}^{-1} \cdot \text{Pa}^{-1})$  which is, as the authors reported, the lowest ever reported for a biodegradable all-polymer LBL assembly.

## References

1. Tharanathan, R. Biodegradable films and composite coatings: Past, present and future. *Trends Food Sci Tech* 14:71–78, 2003.

- 2. Debeaufort, F., Quezada-Gallo, J. A., Voilley, A. Edible films and coatings: Tomorrow's packagings: A review. *Crit Rev Food Sci* 38:299–313, 1998.
- 3. Bucci, D. Z., Tavares, L. B. B., Sell, I. PHB packaging for the storage of food products. *Polym Test* 24: 564–571, 2005.
- 4. Janjarasskul, T., Krochta, J. M. Edible packaging materials. *Annu Rev Food Sci Technol* 1:415–448, 2010.
- 5. Rhim, J. W., Park, H. M., Ha, C. S. Bio-nanocomposites for food packaging applications. *Prog Polym Sci* 38:1629–1652, 2013.
- 6. Averous, L., and Boquillon, N. Biocomposites based on plasticized starch: Thermal and mechanical behaviors. *Carbohydr Polym* 56:111–122, 2004.
- Mali, S., Sakanaka, L. S., Yamashita, F., Grossmann, M. V. E. Water sorption and mechanical properties of cassava starch films and their relation to plasticizing effect. *Carbohydr Polym* 60:283–289, 2005.
- Ghanbarzadeh, B., Almasi, H., Entezami, A. A. Physical properties of edible modified starch/carboxymethyl cellulose films. *Innov Food Sci Emerg Technol* 11:697–702, 2010.
- 9. Tajik, S., Maghsoudlou, Y., Jafari, S. M., Khodaiyan, F., Ghasemlou, M., Aalami, M. Soluble soybean polysaccharide: A new carbohydrate to make a biodegradable film for sustainable green packaging. *Carbohydr Polym* 97:817–824, 2013.
- Bravin, B., Peressini, D., Sensidoni, A. Development and application of polysaccharide-lipid edible coating to extend shelf-life of dry bakery products. *J Food Eng* 76:280–290, 2006.
- 11. Jiménez, A., Fabra, M. J., Talens, P., Chiralt, A. Effect of re-crystallization on tensile, optical and water vapour barrier properties of corn starch films containing fatty acids. *Food Hydrocolloid* 26:302–310, 2012.
- 12. Schmidt, C. V. R., Porto, L. M., Laurindo, J. B., Menegalli, F. C. Water vapour barrier and mechanical properties of starch films containing stearic acid. *Ind Crop Prod* 41:227–234, 2013.
- Arvanitoyannis, I. S., Dionisopoulou, N. K. Irradiation of edible films of plant and animal origin. In *Irradiation of Food Commodities: Techniques, Applications, Detection, Legislation, Safety and Consumer Opinion*, ed. I. S. Arvanitoyannis, pp. 609–634, London: Elsevier-Academic Press, 2010.
- 14. Rogovina, S., Aleksanyan, K., Prut, E., Gorenberg, A. Biodegradable blends of cellulose with synthetic polymers and some other polysaccharides. *Eur Polym J* 49:194–202, 2013.
- Abugoch, L. E., Tapia, C., Villamán, M. C., Yazdani-Pedram, M., Díaz-Dosque, M. Characterization of quinoa protein-chitosan blend edible films. *Food Hydrocolloid* 25:879–886, 2011.
- 16. Muscat, D., Adhikari, B., Adhikari, R., Chaudhary, D. S. Comparative study of film forming behaviour of low and high amylose starches using glycerol and xylitol as plasticizers. *J Food Eng* 109:189–201, 2012.
- 17. De Moura, M. R., Aouada, F. A., Avena-Bustillos, R. J., McHugh, T. H., Krochta, J. M., Mattoso, L. H. C. Improved barrier and mechanical properties

of novel hydroxypropyl methylcellulose edible films with chitosan/tripoly-phosphate nanoparticles. *J Food Eng* 92:448–453, 2009.

- Rodriguez, M., Oses, J., Ziani, K., Mate, J. I. Combined effect of plasticizers and surfactants on the physical properties of starch based edible films. *Food Res Int* 39:840–846, 2006.
- Romero-Bastida, C. A., Bello-Pérez, L. A., Garcia, M. A., Martino, M. N., Solorza-Feria, J., Zaritzky, N. E. Physicochemical and microstructural characterization of films prepared by thermal and cold gelatinization from nonconventional sources of starches. *Carbohydr Polym* 60:235–244, 2005.
- Krochta, J. M., and De Mulder-Johnston, C. Edible and biodegradable polymer films: Challenges and opportunities. *Food Technol-Chicago* 51:61–74, 1997.
- 21. Kester, J., and Fennema, O. R., Edible films and coatings: A review. *Food Technol-Chicago* 40:47–59, 1986.
- 22. Rhim, J. W. Physical and mechanical properties of water resistant sodium alginate films. *LWT-Food Sci Technol* 37:323–330, 2004.
- Hambleton, A., Debeaufort, F., Bonnotte, A., Voilley, A. Influence of alginate emulsion-based films structure on its barrier properties and on the protection of microencapsulated aroma compound. *Food Hydrocolloid* 23:2116– 2124, 2009.
- Nieto, M. B. Structure and function of polysaccharide gum-based edible films and coatings. In *Edible Films and Coatings for Food Applications*, eds. M. E. Embuscado, K. C. Huber, pp. 57–112. Springer, 2009.
- Fabra, M. J., Hambleton, A., Talens, P., Debeaufort, F., Chiralt, A. Voilley, Influence of interactions on water and aroma permeabilities of ι-carrageenanoleic acid-beeswax films used for flavour encapsulation. *Carbohydr Polym* 76:325–332, 2009.
- Muzzarelli, R. A. A. Chitosan-based dietary foods. *Carbohydr Polym* 29:309– 316, 1996.
- Díaz-Sobac, R., García, H. S., Beristain, C. I., Vernon-Carter, E. J. Morphology and water vapour permeability of emulsion films based on mesquite gum. J Food Process Pres 26:129–141, 2002.
- Soares, R. M. D., Lima, A. M. F., Oliveira, R. V. B., Pires, A. T. N., Soldi, V. Thermal degradation of biodegradable edible films based on xanthan and starches from different sources. *Polym Degrad Stabil* 90:449–454, 2005.
- 29. Xu, X., Li, B., Kennedy, J. F., Xie, B. J., Huang, M. Characterization of konjac glucomannan-gellan gum blend films and their suitability for release of nisin incorporated therein. *Carbohydr Polym* 70:192–197, 2007.
- Piermaria, J. A., Pinotti, A., García, M. A., Abraham, A. G. Films based on kefiran, an exopolysaccharide obtained from kefir grain: Development and characterization. *Food Hydrocolloid* 23:684–690, 2009.
- Rimada, P. S., and Abraham, A. G. Kefiran improves rheological properties of glucono-δ-lactone induced skim milk gels. *Int Dairy J* 16:33–39, 2006.

- 32. Piermaria, J. A., de la Canal, M., Abraham, A. Gelling properties of kefiran, a food grade polysaccharide obtained from kefir grain. *Food Hydrocolloid* 22:1520–1527, 2008.
- Nisperos-Carriedo, M. Edible coating based on polysaccharides. In *Edible Coatings and Films to Improve Food Quality*, eds. J. M. Krochta, E. Baldwin, M. O. Nisperos-Carriedo, pp. 201–277. Lancaster: Technomic Publishing, 1994.
- Lacroix, M. and Le Tien, C. Edible films and coatings from non-starch polysaccharides. In *Innovations in Food Packaging*, ed. J. H. Han, pp. 338–361. London: Elsevier Academic Press, 2005.
- Paes, S. S., Yakimets, I., Mitchell, J. R. Influence of gelatinization process on functional properties of cassava starch films. *Food Hydrocolloid* 22:788–797, 2008.
- López, O. V., García, M. A., Zaritzky, N. E. Film forming capacity of chemically modified corn starches. *Carbohydr Polym* 73:573–581, 2008.
- 37. Pagella, C., Spigno, G., De Faveri, D. M. Characterization of starch based edible coatings. *Food Bioprod Process* 80:193–198, 2002.
- Liu, Z. Edible films and coatings from starches. In *Innovations in Food Packaging*, ed. J. H. Han, pp. 318–337. London: Elsevier Academic Press, 2005.
- 39. Protzman, T. F., Wagoner, J. A., Young, A. H. US Patent No. 3344216, 1967.
- 40. Muetgeert, J., Bus, W. C., Hiemstra, P. Influence of formaldehyde on viscosity stability of concentrated aqueous amylose solutions. *J Chem Eng Data* 7:272–276, 1962.
- 41. Wolff, I. A., Davis, H. A., Cluskey, J. E., Gundrum, L. J., Rist, C. E., Preparation of films from amylose. *Ind Eng Chem Res* 43:915–919, 1951.
- Choi, J. H., Choi, W. Y., Cha, D. S., Chinnan, M. J., Park, H. J., Lee, D. S., Park, J. M. Diffusivity of potassium sorbate in κ-carrageenan based antimicrobial film. *LWT-Food Sci Technol* 38:417–423, 2005.
- Hambleton, A., Debeaufort, F., Beney, L., Karbowiak, T., Voilley, A. Protection of active aroma compound against moisture and oxygen by encapsulation in biopolymeric emulsion-based edible films. *Biomacromolecules* 9:1058–1063, 2008.
- 44. Fabra, M. J., Talens, P., Chiralt, A. Effect of alginate and  $\lambda$ -carrageenan on tensile properties and water vapour permeability of sodium caseinate-lipid based films. *Carbohydr Polym* 74:419–426, 2008.
- 45. Pavlath, A. E., Gosset, C., Camirand, W., Robertson, H. Ionomeric films of alginic acid. *J Food Sci* 64:61–63, 1999.
- Nussinovitch, A., and Hershko, V. Gellan and alginate vegetable coatings. *Carbohydr Polym* 30:185–192, 1996.
- 47. Cha, D. S., Choi, J. H., Chinnan, M. S., Park, H. J. Antimicrobial films based on Na-alginate and k-carrageenan. *LWT-Food Sci Technol* 35:715–719, 2002.

- 48. Immirzi, B., Santagata, G., Vox, G., Schettini, E. Preparation, characterization and field-testing of a biodegradable sodium alginate-based spray mulch. *Biosystems Eng* 102:461–472, 2009.
- 49. Conca, K. R., and Yang, T. C. S. Edible food barrier coatings. In *Biodegradable Polymers and Packaging*, eds. C. Ching, D. Kaplan, E. Thomas, pp. 357–369. Lancaster: Technomic Publishing, 1993.
- Maftoonazad, N., Ramaswamy, H. S., Marcotte, M. Evaluation of factors affecting barrier, mechanical and optical properties of pectin-based films using response surface methodology. *J Food Process Eng* 30:539–563, 2007.
- 51. Tharanathan, R. N., and Kittur, F. S. Chitin-the undisputed biomolecule of great potential. *Crit Rev Food Sci* 43:61–87, 2003.
- 52. Hosokawa, J., Nishiyama, M., Yashihora, K., Kuba, T. Biodegradable film derived from chitosan and homogenized cellulose. *Ind Eng Chem Res* 29:800–805, 1990.
- 53. Anker, M. *Edible and biodegradable films and coatings for food packaging A literature review*, SIK-Report. No: 623: Goteborg, Sweden, 1996.
- 54. Butler, B. L., Vergano, P. J., Testin, J. M., Bunn, J. M., Wiles, J. L. Mechanical and barrier properties of edible chitosan films as affected by composition and storage. *J Food Sci* 61:953–955, 1996.
- 55. Caner, C., Vergano, P. J., Wiles, J. L. Chitosan film mechanical and permeation properties as affected by acid, plasticizer and storage. *J Food Sci* 68:1049–1053, 1998.
- El Ghaouth, A., Arul, J., Ponnampalam, R., Boulet, M. Chitosan coating effect on storability and quality of fresh strawberries. *J Food Sci* 56:1618– 1631, 1991.
- El Ghaouth, A., Arul, J., Wilson, C., Benhamou, N. Ultrastructural and cytochemical aspects of the effect of chitosan on decay of bell pepper fruit. *Physiol Mol Plant P* 44:417–432, 1994.
- Chen, M. C., Yeh, G. H. C., Chiang, B. H. Antimicrobial and physicochemical properties of methylcellulose and chitosan films containing a preservative. *J Food Process Pres* 20:379–390, 1996.
- Tsai, G. J., Wu, Z. Y., Su, W. H. Antibacterial activity of a chitooligosaccharide mixture prepared by cellulase digestion of shrimp chitosan and its application to milk preservation. *J Food Prot* 63:747–752, 2000.
- Coma, V., Martial-Gros, A., Garreau, S., Copinet, A., Salin, F., Deschamps, A. Edible antimicrobial films based on chitosan matrix. *J Food Sci* 67:1162– 1169, 2002.
- Dutta, P. K., Tripathi, S., Mehrotra, G. K., Dutta, J. Perspectives for chitosan based antimicrobial films in food applications. *Food Chem* 114:1173–1182, 2009.
- 62. Phan, T. D., Debeaufort, F., Voilley, A., Luu, D. Biopolymer interactions affect the functional properties of edible films based on agar, cassava starch and arabinolyxan blends. *J Food Eng* 90:548–558, 2009.
- 63. Yuen, S. Pullulan and its applications. Process Biochem 9:7-9, 1974.

- 64. Kristo, E., Biliaderis, C. G. Water sorption and thermo-mechanical properties of water/sorbitol-plasticized composite biopolymer films: Caseinatepullulan bilayers and blends. *Food Hydrocolloid* 20:1057–1071, 2006.
- Gounga, M. E., Xu, S. Y., Wang, Z. Whey protein isolate based edible films as affected by protein concentration, glycerol ratio and pullulan addition in film formation. *J Food Eng* 83:521–530, 2007.
- Kristo, E., Biliaderis, C. G., Zampraka, A. Water vapour barrier and tensile properties of composite caseinate-pullulan films: Biopolymer compositions effects and impact of beeswax lamination. *Food Chem* 101:753–764, 2007.
- 67. Tong, Q., Xiao, Q., Lim, L. T. Preparation and properties of pullulan-alginate-carboxymethylcellulose blend films. *Food Res Int* 41:1007–1014, 2008.
- 68. León, P. G., and Rojas, A. M. Gellan gum films as carriers of l-(+)-ascorbic acid. *Food Res Int* 40:565–575, 2007.
- 69. Yang, L., Paulson, A. T. Mechanical and water vapour barrier properties of edible gellan films. *Food Res Int* 33:563–570, 2000.
- Akhtar, M. J., Jacquot, M., Jamshidian, M., Imran, M., Arab-Tehrany, E., Desobry, S. Fabrication and physical characterization of HPMC films with commercial plant extract: Influence of light and film composition. *Food Hydrocolloid* 31:420–427, 2013.
- 71. Ahmadi, E., Sareminezhad, S., Azizi, M. H. The effect of ultrasound treatment on some properties of methylcellulose films. *Food Hydrocolloid* 25:1399–1401, 2011.
- Bonilla, J., Atarés, L., Vargas, M., Chiralt, A. Properties of wheat starch filmforming dispersions and films as affected by chitosan addition. *J Food Eng* 114:303–312, 2013.
- 73. Galus, S., and Lenart, A. Development and characterization of composite edible films based on sodium alginate and pectin. *J Food Eng* 115:459–465, 2013.
- Jiménez, A., Fabra, M. J., Talens, P., Chiralt, A. Influence of hydroxypropylmethylcellulose addition and homogenization conditions on properties and ageing of corn starch based films. *Carbohydr Polym* 89:676–686, 2012b.
- 75. Park, S. Y., Lee, B. I., Jung, S. T., Park, H. J. Biopolymer composite films based on κ-carrageenan and chitosan. *Mater Res Bull* 36:511–519, 2001.
- Tapia, M. S., Rojas-Graü, M. A., Rodríguez, F. J., Ramírez, J., Carmona, A., Martín-Belloso, O. Alginate- and gellan-based edible films for probiotic coatings on fresh-cut fruits. *J Food Sci* 72:190–196, 2007.
- Shellhammer, T. H., and Krochta, J. M. Edible coating and film barriers. In *Lipids-Industrial Applications and Technology*, eds. F. D. Gunstone, F. B. Padley, pp. 453–479. New York: Marcel Dekker, 1997.
- Anonymous. A food technologist's guide to Methocel premium food gums. The Dow Chemical Co., Midland, MI, USA, 1990.
- Araujo-Farro, P. C., Podadera, G., Sobral, P. J. A., Menegalli, F. C. Development of films based on quinoa (Chenopodium quinoa, Willdenow) starch. *Carbohydr Polym* 81:839–848, 2010.

- 80. Park, H. J., and Chinnan, M. S. Gas and water vapor barrier properties of edible films from protein and cellulosic materials. *J Food Eng* 25:497–507, 1995.
- Wu, Y., Geng, F., Chang, P. R., Yu, J., Ma, X. Effect of agar on the microstructure and performance of potato starch film. *Carbohydr Polym* 76:299–304, 2009.
- 82. Hanlon, J. F. Films and foils. In *Technomic: Handbook of Package Engineering*, ed. J. F. Hanlon, pp. 3.1–3.59. Lancaster: Technomic Publishing, 1992.
- 83. Salame, M. Barrier polymers. In *The Wiley Encyclopedia of Packaging Technology*, ed. M. Bakker, pp. 48–54. New York: Wiley, 1986.
- 84. Almasi, H., Ghanbarzadeh, B., Entezami, A. A. Physicochemical properties of starch-CMC-nanoclay biodegradable films. *Int J Biol Macromol* 46:1–5, 2010.
- Briston, J. H. Films, plastic. In *The Wiley Encyclopedia of Packaging Technology*, ed. M. Bakker, pp. 329–335. New York: Wiley, 1986,
- Bergo, P. V. A., Carvalho, R. A., Sobral, P. J. A., dos Santos, R. M. C., da Silva, F. B. R., Prison, J. M., *et al.*, Physical properties of edible films based on cassava starch as affected by the plasticizer concentration. *Packag Technol Sci* 21:85–89, 2008.
- 87. Iijima, M., Nakamura, K., Hatakeyama, T., Hatakeyama, H. Phase transition of pectin with sorbed water. *Carbohydr Polym* 41:101–106, 2000.
- 88. Jiménez, A., Fabra, M. J., Talens, P., Chiralt, A. Phase transitions in starch based films containing fatty acids: Effect on water sorption and mechanical behaviour. *Food Hydrocolloid* 30:408–418, 2013a.
- Martínez-Camacho, A. P., Cortez-Rocha, M. O., Ezquerra-Brauer, J. M., Graciano-Verdugo, A. Z., Rodríguez-Félix, F., Castillo-Ortega, M. M., Yépiz-Gómez, M. S., Plascencia-Jatomea, M. Chitosan composite films: Thermal, structural, mechanical and antifungal properties. *Carbohydr Polym* 82:305– 315, 2010.
- Sudhamani, S. R., Prasad, M. S., Udaya Sankar, K. DSC and FTIR studies on gellan and polyvinyl alcohol (PVA) blend films. *Food Hydrocolloid* 17:245– 250, 2003.
- Xiao, Q., Lim, L. T., Tong, Q. Preparation of pullulan-based blend films as affected by alginate content and relative humidity. *Carbohydr Polym* 87:227– 234, 2012.
- Marcos, B., Aymerich, T., Monfort, J., Garriga, M. Use of antimicrobial biodegradable packaging to control Listeria monocytogenes during storage of cooked ham. *Int J Food Microbiol* 120:152–158, 2007.
- Navarro-Tarazaga, M. L., Massa, A., Pérez-Gago, M. B. Effect of beeswax content on hydroxypropyl methylcellulose-based edible film properties and postharvest quality of coated plums (cv. Angeleno). *LWT-Food Sci Technol* 44:2328–2334, 2011.
- Cannarsi, M., Baiano, A., Marino, R., Sinigaglia, M., Del Nobile, M. A. Use of biodegradable films for fresh cut beef steaks packaging. *Meat Sci* 70:259–265, 2005.

- 95. Mei, J., Yuan, Y., Wu, Y., Li, Y. Characterization of edible starch-chitosan film and its application in the storage of mongolian cheese. *Int J Biol Macromol* 57:17–21, 2013.
- 96. Jiménez, A., Fabra, M. J., Talens, P., Chiralt, A. Edible and biodegradable starch films: A review. *Food Bioprocess Technol* 5:2058–2076, 2012c.
- Arvanitoyannis, I., Psomiadou, E., Nakayama, A., Aiba, S., Yamamoto, N. Edible films made from gelatin, soluble starch and polyols: Part 3. *Food Chem* 60:593–604, 1997.
- Sothornvit, R., and Krochta, J. M. Plasticizer effect on mechanical properties of beta-globulin (β-Lg) films. *J Food Eng* 50:149–155, 2001.
- Talja, R. A., Helén, H., Roos, Y. H., Jouppila, K. Effect of type and content of binary polyol mixtures on physical and mechanical properties of starchbased edible films. *Carbohydr Polym* 71:269–276, 2008.
- Quezada-Gallo, J. A., Debeaufort, F., Callegarin, F., Voilley, A. Lipid hydrophobicity, physical state and distribution effects on the properties of emulsion-based edible films. *J Membrane Sci* 180:37–46, 2000.
- Jiménez, A., Fabra, M. J., Talens, P., Chiralt, A. Effect of lipid self-association on the microstructure and physical properties of hydroxypropyl-methylcellulose edible films containing fatty acids. *Carbohydr Polym* 82:585–593, 2010.
- 102. Xu, Y. X., Kim, K. M., Hanna, M. A., Nag, D. Chitosan-starch composite film: Preparation and characterization. *Ind Crop Prod* 21:185–192, 2005.
- 103. Mathew, S., and Abraham, T. E. Characterisation of ferulic acid incorporated starch-chitosan blend films. *Food Hydrocolloid* 22:826–835, 2008.
- 104. Kou, W., Cai, C., Xu, S., Wang, H., Liu, J., Yang, D., *et al.*, In vitro and in vivo evaluation of novel immediate release carbamazepine tablets: Complexation with hydroxypropyl-β-cyclodextrin in the presence of HPMC. *Int J Pharm* 409:75–80, 2011.
- 105. Annable, P., Fitton, M. G., Harris, B., Philips, G. O., Williams, P. A. Phase behaviour and rheology of mixed polymer systems containing starch. *Food Hydrocolloid* 8:351–359, 1994.
- 106. Rivero, S., García, M. A., Pinotti, A. Crosslinking capacity of tannic acid in plasticized chitosan films. *Carbohydr Polym* 82:270–276, 2010.
- 107. Reddy, N., and Yang, Y. Citric acid cross-linking of starch films. *Food Chem* 3:702–711, 2010.
- Rhim, J. W., and Wang, L. F. Mechanical and water barrier properties of agar/κ-carrageenan/konjac glucomannan ternary blend biohydrogel films. *Carbohydr Polym* 96:71–81, 2013.
- 109. Kopeček, J., and Yang, J. Hydrogels as smart biomaterials. *Polym Int* 56:1078–1098, 2007.
- 110. Farris, S., Schaich, K. M., Liu, L., Piergiovanni, L., Yam, K. L. Development of polyion-complex hydrogels as an alternative approach for the production of bio-based polymers for food packaging applications: A review. *Trends Food Sci Tech* 20:316–332, 2009.

- 111. Lee, K. Y., Shim, J., Lee, H. G. Mechanical properties of gellan and gelatin composite films. *Carbohydr Polym* 56:251–254, 2004.
- 112. Wongsasulak, S., Yoovidhya, T., Bhumiratana, S., Hongsprabhas, P., McClements, D. J., Weiss, J. Thermo-mechanical properties of egg albumencassava starch composite films containing sunflower-oil droplets as influenced by moisture content. *Food Res Int* 39:277–284, 2006.
- Osés, J., Fabregat-Vázquez, M., Pedroza-Islas, R., Tomás, S. A., Cruz-Orea, A., Maté, J. I. Development and characterization of composite edible films based on whey protein isolate and mesquite gum. *J Food Eng* 92:56–62, 2009.
- 114. Wang, L., Auty, M. A. E., Kerry, J. P. Physical assessment of composite biodegradable films manufactured using whey protein isolate, gelatin and sodium alginate. *J Food Eng* 96:199–207, 2010.
- 115. Harper, B. A., Barbut, S., Lim, L. T., Marcone, M. F. Characterization of 'wet' alginate and composite films containing gelatin, whey or soy protein. *Food Res Int* 52:452–459, 2013.
- Jiménez, A., Fabra, M. J., Talens, P., Chiralt, A. Effect of sodium caseinate on properties and ageing behaviour of corn starch based films. *Food Hydrocolloid* 29:265–271, 2012d.
- 117. Jiménez, A., Fabra, M. J., Talens, P., Chiralt, A. Physical properties and antioxidant capacity of starch-sodium caseinate films containing lipidsm. *J Food Eng* 116:695–702, 2013b.
- 118. Rhim, J. W., Hong, S. I., Park, H. M., Perry, K. W. N. Preparation and characterization of chitosan-based nanocomposite films with antimicrobial activity. *J Agr Food Chem* 54:5814–5822, 2006.
- 119. Rhim, J. W. Effect of clay contents on mechanical and water vapour barrier properties of agar-based nanocomposite films. *Carbohydr Polym* 86:691–699, 2011.
- 120. Abdollahi, M., Alboofetileh, M., Rezaei, M., Behrooz, R. Comparing physico-mechanical and thermal properties of alginate nanocomposite films reinforced with organic and/or inorganic nanofillers. *Food Hydrocolloid* 32:416–424, 2013.
- Bilbao-Sainz, C., Bras, J., Williams, T., Sénechal, T., Orts, W. HPMC reinforced with different cellulose nano-particles. *Carbohydr Polym* 86:1549–1557, 2011.
- 122. Chang, P. R., Jian, R., Yu, J., Ma, X. Starch-based composites reinforced with novel chitin nanoparticles. *Carbohydr Polym* 80:420–425, 2010.
- 123. Famá, L. M., Pettarin, V., Goyanes, S. N., Bernal, C. R. Starch/multi-walled carbon nanotubes composites with improved mechanical properties. *Carbohydr Polym* 83:1226–1231, 2011.
- 124. Zhang, H. Y., Tehrany, E. A., Kahn, C. J. F., Ponçot, M., Linder, M., Cleymand, F. Effets of nanoliposomes based on soya, rapeseed and fish lecithins on chitosan thin films designed for tissue engineering. *Carbohydr Polym* 88:618– 627, 2012.

- 125. Jiménez, A., Sánchez-González, L., Desobry, S., Chiralt, A., Arab Tehrany, E. Influence of nanoliposomes incorporation on properties of film forming dispersions and films based on corn starch and sodium caseinate. *Food Hydrocolloid* 35:159–169, 2013c.
- Cyras, V., Manfredi, L. B., Ton-That, M. T., Vázquez, A. Physical and mechanical properties of thermoplastic starch/montmorillonite nanocomposite films. *Carbohydr Polym* 73:55–63, 2008.
- 127. Park, H. M., Lee, W. K., Park, C. Y., Cho, W. J., Ha, C. S. Environmentally friendly polymer hybrids. Part I: Mechanical, thermal and barrier properties of thermoplastic starch/clay nanocomposites. *J Mater Sci* 38:909–915, 2003.
- 128. Alexandre, M., Dubois, P. Polymer-layered silicate nanocomposites: Preparation, properties and uses of a new class of materials. *Mater Sci Eng* 28:1-63, 2000.
- 129. Shukla, M. K., Singh, R. P., Reddy, C. R. K., Jha, B. Synthesis and characterization of agar-based silver nanoparticles and nanocomposite film with antibacterial applications. *Bioresource Technol* 107:295–300, 2012.
- 130. Travan, A., Pelillo, C., Donati, I., Marsich, E., Benincasa, M., Scarpa, T., Semeraro, S., Turco, G., Gennaro, R., Paoletti, S. Non-cytotoxic silver nanoparticle-polysaccharide nanocomposites with antimicrobial activity. *Biomacromolecules* 10:1429–1435, 2009.
- 131. Falguera, V., Quintero, J. P., Jiménez, A., Aldemar Muñoz, J., Ibarz, A. Edible films and coatings: Structures, active functions and trends in their use. *Trends Food Sci Tech* 22:292–303, 2011.
- García, M. A., Ferrero, C., Bértola, N., Martino, M., Zaritzky, N. Edible coatings from cellulose derivatives to reduce oil uptake in fried products. *Innov Food Sci Emerg Technol* 3:391–397, 2002.
- 133. Gol, N. B., Chaudhari, M. L., Ramana Rao, T. V. Effect of edible coatings on quality and shelf life of carambola (Averrhoa carambola L.) fruit during storage. *J Food Sci Technol* 2013; doi:10.1007/s13197-013-0988-9.
- 134. Lago-Vanzela, E. S., do Nascimento, P., Fontes, E. A. F., Mauro, M. A., Kimura, M. Edible coatings from native and modified starches retain carotenoids in pumpkin during drying. *LWT-Food Sci Technol* 50:420–425, 2013.
- 135. Maqbool, M., Ali, A., Ramachandran, S., Smith, D. R., Alderson, P. G. Control of postharvest anthracnose of banana using a new edible composite coating. *Crop Prot* 29:1136–1141, 2010.
- 136. Mohebbi, M., Ansarifar, E., Hasanpour, N., Amiryousefi, M. R. Suitability of aloe vera and gum tragacanth as edible coatings for extending the shelf life of button mushroom. *Food Bioprocess Technol* 5:3193–3202, 2012.
- 137. Perdones, A., Sánchez-González, L., Chiralt, A., Vargas, A. Effect of chitosan-lemon essential oil coatings on storage-keeping quality of strawberry. *Postharvest Biol Tec* 70:32–41, 2012.
- 138. Ponce, A. G., Roura, S. I., del Valle, C. E., Moreira, M. R. Antimicrobial and antioxidant activities of edible coatings enriched with natural plant extracts: In Vitro and in vivo studies. *Postharvest Biol Tec* 49:294–300, 2008.

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- 139. Robles-Sánchez, R. M., Rojas-Graü, M. A., Odriozola-Serrano, I., González-Aguilar, G., Martín-Belloso, O. Influence of alginate-based edible coating as carrier of antibrowning agents on bioactive compounds and antioxidant activity in fresh-cut Kent mangoes. *LWT-Food Sci Technol* 50:240–246, 2013.
- 140. Schreiber, S. B., Bozell, J. J., Hayes, D. G., Zivanovic, S. Introduction of primary antioxidant activity to chitosan for application as a multifunctional food packaging material. *Food Hydrocolloid* 33:207–214, 2013.
- 141. Gu, C. H., Wang, J. J., Yu, Y., Sun, H., Shuai, N., Wei, B. Biodegradable multilayer barrier films based on alginate/polyethyleneimine and biaxially oriented poly (lactic acid). *Carbohydr Polym* 92:1579–1585, 2013.
- 142. Laufer, G., Kirkland, C., Cain, A. A., Grunlan, J. C. Oxygen barrier of multilayer thin films comprised of polysaccharides and clay. *Carbohydr Polym* 95:299–302, 2013.
- 143. Singthong, J., Thongkaew, C. Using hydrocolloids to decrease oil absorption in banana chips. *LWT-Food Sci Technol* 42:1199–1203, 2009.
- 144. Koch, C. A., Akhave, J. R., Bharadwaj, R. K. Layer by layer assembled nanocomposite barrier coatings. Google Patents. 2013.

## Food Packaging for High Pressure Processing

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#### Abstract

High pressure processing (HPP) of foods mainly utilizes flexible packaging materials for commercial products. Many materials have been evaluated for their adequacy in the process. There are a number of integrity, design and high-pressure process control requirements for these packaging materials that must be complied with for acceptance and use in different product applications. These include gas permeability, seal and physical strength properties, and global migration of packaging components into the food, some of which are specific to either refrigerated or shelf-stable products. Laminate options reported in the literature were reviewed and suitable packaging materials for HPP at both low- and high-temperature conditions were classified. Packs with a gaseous headspace (modified atmosphere packaging = MAP) are especially challenging due to the large volume compression under high pressure and because of the behavior of gaseous headspace mixtures under variable HPP conditions. For example, some materials encountered problems during HPP including morphological changes, delamination and microdefects of films and foodstuff. This chapter highlights a selection of suitable combinations of materials, package design and HPP parameters, in particular product applications and packaging materials currently utilized in industry. Criteria to assess deviations of packaging materials after HPP are discussed in view of further harmonization being required for the adequacy of tests for reliable packaging selection.

*Keywords:* Food packaging, high pressure, thermal, polymers, films, containers, processing

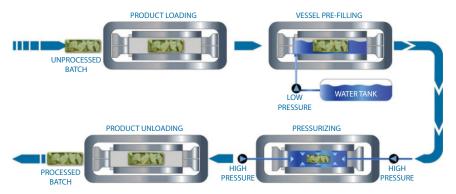
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## 8.1 High Pressure Processing of Foods

High pressure processing (HPP) is an innovative technology applied for food safety assurance, shelf-life extension, and nutrient preservation. Food items are prepackaged into flexible containers and loaded into a cylindrical hydrostatic pressurization vessel (Figure 8.1). The vessel is then closed and filled with compression fluid (typically water) and pressurization starts via further pumping of fluid until reaching target pressures between 200 and 800 MPa. The pressure selection will depend upon product application. Food containers remain under pressure for a period of time (ranging from seconds up to over 20 min, generally up to 5 min) and pressure is released for product unloading. Especially for the treatment of MAP packages, the pressure release gradient is controlled depending upon product application. Subsequently the packages are typically dried, labeled or printed—if non-water-resistant or pressure stable labels or print are required—and packed into secondary packaging for storage and distribution.

High pressure processing is known for its potential in manufacturing value-added foods, retaining heat-labile nutrients, flavors, and aromas, with products ranging from individual to institutional size packages (e.g., 6 kg sliced turkey breast package). This technology is advantageous for the uniform and almost instant pressure transmission inside the product and for nutrient and volatile retention resulting from the use of low to milder temperatures. Precooling or preheating of products and temperature equilibration are important steps in HPP to achieve the required process temperature. The commercial process temperature generally ranges from chilled temperatures (4°C) to above ambient temperatures (up to 50°C), although this technology is also explored for freezing and cooling and



**Figure 8.1** Description of an industrial high pressure process. Source: Carole Tonello-Samson, Hiperbaric, with permission.

thermal sterilization. Commercial processes currently often use 600 MPa for product pasteurization or shelf-life extension via microbial and enzymatic load reduction, which will require storage at refrigerated conditions. Other vessels currently existing at pilot scale are designed to pressurize preheated food packages, working with heated vessel walls and pressurization water, to enable microbial spore inactivation and thereby achieve low acid food product stability and extended storage at chilled or ambient conditions. Manufacturing of chilled meals requires a pressurization temperature near 90°C at 600 MPa, while sterilized (ambient storage) products will require temperatures higher than 105°C when using this pressure.

The US Food and Drug Administration (FDA) and Department of Agriculture (USDA) have approved HPP as a post-package pasteurization technology for manufacture of shelf-stable high-acid foods and pasteurized low-acid food products, and developed guidelines and regulations for those products (21CFR §114 and 21CFR§113). In 2009, the US FDA approved the first petition for the commercial use of pressure-assisted thermal sterilization (PATS) for application in the production of a mashed potato product in a 35 L high pressure sterilization vessel. Earlier, the European Commission on food regulations adapted existing legislation on novel foods to products processed by HPP (EC258/97; European Commission, 2002) and later, Health Canada (Novel Food Decisions, available on Health Canada's website: http://www.novelfoods.gc.ca) issued "no-objections novel foods decisions" concerning ready-to-eat meat and poultry products, which have been treated by HPP for the control of Listeria monocytogenes (2006), as well as for meat-containing entrees, meat-containing salads and meat products (2006), and applesauce and apple sauce/fruit blends (2004).

Even though HPP is mainly a batch or semi-batch process, semi-continuous and continuous systems are currently also commercially available. However, semi-continuous HPP systems are used only in a few cases to directly process pumpable products, which then need to be aseptically packaged. Batch or semi-batch processing vessels are most commonly found in the food industry and require prepackaged products. Commonly, the food and its packaging are treated together; thus the entire package remains a secure unit until the consumer opens it.

In order to achieve a quasi-continuous product flow of prepackaged products, several automation concepts have been developed. Some of them are based on the tandem concept, the alternating usage of multiple HPP vessels integrated in a packaging and HPP production line with a single control system [1].

# 8.2. Commercial HPP Applications and Packaging Formats

In-container HPP requires packages in the form of multilayer pouches, large bulk bags, container-lid tray combinations, and polymeric bottles (see commercial examples in Figure 8.2). In 2012, more than 350,000 tonnes of food packages were produced by HPP by more than 100 companies using more than 230 HPP machines globally [2]. A number of commercial products such as sliced meats, vegetables and salsa dips, fruit juices, seafood products, and ready-to-eat chilled products processed by applying HPP are available today in the worldwide market.

Packaging materials, which are oxygen-impermeable and opaque to light, have been developed to keep colors and flavors fresh in certain highpressure-treated foods and to inhibit microbial growth. Some multilayer structures with functional or high-barrier properties may also be suitable for prepackaged HPP foods.



Multilayer pouches



Figure 8.2 Container types used for commercial high-pressure products.

A number of requirements define the packaging integrity and barrier properties and must be met during and after processing to ensure preservation of high-pressure-treated food throughout its shelf life; these include: flexibility, visual integrity, gas and water vapor barrier properties, laminate bonding and seal strength, headspace gas mixture and process control, adequate heat transfer properties, material aging, printability and transparency, and migration limits.

- HPP requires flexible and semi-rigid gastight packages made • of polymers or copolymers that can withstand a change in volume corresponding to the compressibility of the product. Foods decrease in volume as function of the pressure applied and a relatively similar expansion, depending on the material properties, occurs upon decompression. For this reason, the packaging used for vacuum packaged foods must be able to accommodate up to a 19% reduction in volume during HPP. For products package with modified atmosphere (MAP) the reduction in volume is far more dependent on the volume percentage of gaseous headspace incorporated in the package. After HPP, the package has to return to its original volume without loss of seal integrity or barrier properties. At least one interface in the package should be flexible enough to transmit the pressure. Therefore, rigid metal, glass, some plastic containers, or paper board-based packages are not recommended, as they deform irreversibly or tend to fracture under the compressive forces [3,4]. Moreover, packages made of paperboard are not suitable for pressure treatment either, since they can degrade under pressure [3].
- The package should maintain its integrity for visual aesthetics and barrier properties, avoiding delamination, creasing, pinholes, crazing, or other pressure-induced defects. The latter could be distinguished between direct and indirect pressure-induced defects [5]. Delamination not visible to the naked eye but, nevertheless, potentially affecting barrier properties, should also be assessed when developing HPP-specific packaging and processing concepts. Especially MAP products are prone to visual and microdefects when a not suitable high pressure process control, like fast decompression, is used in conjunction with an inappropriate film and package design. Therefore, the packaging should be

evaluated against the background of the intended HPP process and decompression pattern.

- Requirements for gas and water vapor barrier properties depend on the product application and intended storage temperature. Industrial norms allow up to 12% deviation from standard oxygen and water barrier levels [6]. For developing shelf-stable products to be stored above room temperature, the US army has specified a 0.06 ml/m<sup>2</sup>/day oxygen permeability limit and a 0.01 g/m<sup>2</sup>/day water permeability limit. These specifications are required for a shelf life of 3 years at 25°C or 6 months at 37°C. On the other hand, some commercial shelf-stable products require an oxygen permeability value between 0.1 and 0.2 ml/m<sup>2</sup>/day. Retort pouches generally carry a middle aluminium layer (e.g., 7, 9, and 15 µm thick), which functions as a moisture, light, and gas barrier. Retention of strength properties of a material refers to its tensile strength, tear strength, puncture resistance and the seal strength. Industrial norms suggest that deviations in tensile strength, elongation, elasticity modulus, as well as seal strength, must remain within the 25% range for these properties [6]. In this case, a structure that provides extracttight seals, rounded and reinforced edges is required.
- MAP packs contain a gaseous headspace of 30-50%, which is typically a mixture of CO<sub>2</sub> and N<sub>2</sub> or O<sub>2</sub>. However, a gaseous headspace leads to a higher decrease in package volume during HPP compared to vacuum packaging. Consequently the impact on the packaging and risk of damage is higher. Suitable elastic materials and package shapes are required.
- The package is expected to allow for fast cooling or preheating of the product. Foil laminated materials may provide faster preheating than polymeric materials due to higher thermal conductivity of the aluminum layer in the pouch [7].
- Additional desirable properties of packaging polymers include good aging properties, printability [8] and transparency [9]. Good barrier polymer-based packaging materials can provide transparency, while aluminum and metalized coating cannot provide visibility to the consumer.
- The material must also not allow the migration of compression fluid or food components through the package or the transfer of packaging components to the food during processing or storage. The required EU limit for global migration

of film components is 10 mg/dm<sup>2</sup>. Other substances of films, like antioxidants, have various specific migration limits. Exemplary studies have shown that neither the global nor the specific migration was altered in an undesired way after HPP [10,11]. Due to the large variability of commercially available film blends the migration of packaging which is intended for HPP should be assessed on a case-by-case basis.

The general requirements for HPP packaging, including integrity, oxygen and water permeability, seal and physical strength, and global migration of components, are summarized in Table 8.1. Not meeting gas permeability and strength property requirements is sufficient for initial rejection and out-screening. Commercial packaging manufacturing norms allow deviations of up to 12% in permeability and 25% deviation in material strength, including seal strength. Table 8.2 lists a number of polymers that have been considered for HPP applications and their oxygen and water permeabilities.

The container types commercially utilized for various product applications (fruits and vegetables, red meat and poultry, fish, and dairy) by a number of companies in Australia, Germany, New Zealand, and the USA have been summarized in Table 8.3. These are HPP products utilizing low temperature (<10°C), including refrigerated ready-to-eat meals. In this case, single and combinations of PET, PE, PP and EVOH are common materials composing trays, bottle and flexible pouches. Stand up and resealable pouches are becoming a popular option for high value addition in HPP applications. In general, additional packaging functions such as value-added design, incorporation of intelligent, active or convenience features have become important for HPP marketing. Especially in advancedeconomy countries, there is a clear trend towards resealable MAP trays made by semi-rigid, easy-peel films for more convenience as well as for better visual product presentation in a modified atmosphere package.

## 8.3 Modified Atmosphere Packaging (MAP) for HPP

For a growing population, spare time is becoming a limited resource and consumers appreciate more convenience packaging. In relation to food and nutrition there is an imminent conflict: food should be convenient to handle, store, eat and cook, it should have a long shelf life, but it should be fresh and healthy at the same time.

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Integrity requirement*	HP-low temperature (600 MPa/80°C)*	(600 MPa/80°C)* (800 MPa/133°C)*	Retort (0.2 MPa/ 133°C)*
Visual integrity	no delamination or blistering	no delamination or blistering	no delamination or blistering
Oxygen permeability (maximum deviation 12%)	product dependent	0.06 for US military or 0.5–1.0 ml/m²/day for some commercial products	0.06 for US military or 0.5–1.0 ml/m²/ day for some commercial products
Water permeability (maximum deviation 12%)	product dependent	0.01 g/m²/day or prod- uct dependent	0.01 g/m <sup>2</sup> /day or product dependent
Seal strength properties (maximum deviation 25%)	material dependent	material dependent	seal strength, 2–3.5 kg/100 mm; bond strength 150–500 g/10 ml; burst test 7.5 kg/15 mm seal
Physical strength (tensile, elonga- tion, elasticity modulus; maxi- mum deviation 25%)	material dependent	material dependent	material dependent
Global migration of packaging components to food simulants	< 10 mg/dm <sup>2</sup>	< 10 mg/dm <sup>2</sup>	$< 10 \text{ mg/dm}^2$
Maximum headspace	up to 30%	up to 30%	up to 30%
High thermal conductivity	not required (with exceptions)	required	required
-			

\* Maximum expected pressure/temperature

Polymer	Oxygen permeability at 23°C 50% or 0% RH (ml/m²/day)	Water vapor permeabil- ity at 23°C 85% RH (g/ m²/day)
Ethylene vinyl alcohol (EVOH)	0.001–0.01 (dry)	1-3
Poly (vinylidene chlo- ride) (PVDC)	0.01-0.3	0.1
Poly (vinyl alcohol) (PVAL)	0.02 (dry)	30
Polyamide (PA) or nylon	0.1–1 (dry)	0.5-10
Poly (vinyl chloride) (PVC)	2-8	1-2
Polypropylene (PP)	50-100	0.2-0.4
Polyethylene (PE)	50-200	0.5-2

**Table 8.2** Typical permeability values of polymers that have been used or evaluated for HPP applications (before HPP).

Some of these needs could be addressed by the combination of MAP and HPP. High pressure processing fulfills the requirements to increase food safety, extend shelf life and cater to the consumer preference for food that is as natural as possible without artificial preservatives. Modified atmosphere packaging is commonly used as an additional hurdle and for a superior, more natural presentation of the products within the pack. The MAP packages are gas flushed with a dedicated gas mixture to evacuate significant amounts of air so that the oxygen content in the package is adjusted to the product requirements and sealed with a high barrier film. The oxygen level in the package affects the growth of bacteria, oxidation processes and/or can have an impact on the color of fresh meat. Due to its bacteriostatic properties,  $CO_2$  is also included in the gas mixture. In combination with high pressure it may even provide a synergistic effect on the inactivation rates of bacteria [12,13]. Table 8.4 shows typical MAP gas mixtures suggested for industrial use.

During the pressure ramp-up time a semi-rigid MAP package partly and reversibly collapses due to the compressibility of headspace gas. As shown in Figure 8.3, this could lead to delamination and crazing of composite materials in flexible packages that have a relative large headspace volume [14]. Packages of PA/PE ( $30 \mu m/60 \mu m$ ) filled with CO<sub>2</sub> showed partial delamination by bubble formation and partial loss of transparency after 500 MPa for 5 min [15].

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Table 8.3 Con	nmercial HPP pa	Table 8.3         Commercial HPP packaging by product applications (Hiperbaric, 2010, personal communication).	iperbaric, 2010, personal commu	inication).
Product type	Product	Packaging description	Materials	Example
Fruits and vegetables	Fruit and veg- etable juices	Bottle with screwed caps in few cases with sealed metalized top foil	PETE, PE	PET bottle from Preshafood (Australia)
	Tomato salsa	Cup with sealed top film and stand-up resealable pouches (SURP)	PETE (cup)	Pouch from SimplyFresco (USA)
	Guacamole	Cup and top sealable film and vacuum packed pouch	PP (cup)	Vácuum packed bag from Fresherized Foods (USA)
Meat	Small cooked pork sausages, sliced blood sausages	Preformed tray and top skin film	Darfresh from Cryovac	Espuñ ready to eat tapas
	Cooked sliced meats, sliced bacon, sliced pork meat, small sausages	Skin pack (combined film at top and bottom)	Upper film: PS-EVOH Bottom film: PE-EVOH or Upper film: PE Bottom film: PP	MRM (Spain)
	Whole prosciutto	Vacuum pack metalized bag	PET/Metal/LLDPE or PET/Metal/ Nylon	Abraham Schinken GmbH (Germany)
	Sliced prosciutto	Modified atmosphere packaging	Bottom film: A-PET/PE (PEEL) Top film: PET/PE or BOPP/PE or BOPP/PET/PE)	Abraham Schinken GmbH (Germany)
	Sliced cooked poultry	Zip re-sealable vacuum pack bag		Oscar Mayer (USA)

Product type	Product	Packaging description	Materials	Example
Fish	Ready-to-eat fish meals with	Ready-to-eat fish Preformed tray and top skin film meals with		RTE fish meal from MRM (Spain)
	sauce			
Dairy and other	Sandwich spreads (fresh cheese and mayon- naise based)	Dairy and other     Sandwich spreads     Tray with sealed top film and top Flexible     PET (Tray and top)       (fresh cheese     pouch     and mayon-     and mayon-       naise based)     bottlo induding for the state of the state	PET (Tray and top)	Tray & flexible pouches from Rodilla (Spain) Norr France County
				were minage aroup (were regiantly)

	N <sub>2</sub> content in %	CO <sub>2</sub> content in %	O <sub>2</sub> content in %
Meat, fresh	20-30	0-30	50-70
Meat Products	50-70	30	0-20
Poultry, fresh	30	70	0
Poultry, cooked / smoked	80	20	0
Fish	20-40	30-60	20-30
Seafood	0-70	30-80	0-30
Cheese	20-40	60-80	0
Salads	85-94	4-12	2-3
Fruits	70–95	4-20	1-10

 Table 8.4
 Range of typical gas mixtures for MAP (Source: Multivac).



**Figure 8.3** Delaminaton and micro defects are formed in packaging materials after high pressure processing of 600 MPa, 3 min, due to a unsuitable film and package design combination (Source: Multivac).

The reasons for delamination are the high tensile deformation of the film laminate structure and local temperature hot spots due to the heating of the gases upon compression. Flexible, high-barrier films with an organic barrier layer, like PET/PE/EVOH/PE, could be used for this kind of application. Unlike the common "retort-shock" problem of EVOH-based films like PP/EVOH/PP (100/10/100  $\mu$ m), the barrier properties are not significantly altered after HPP (400 and 800 MPa; 40 and 75°C; 5 and 10 min) [16].

The package design of semi-rigid MAP packs has to be adopted to accommodate the volume reduction as well. To prevent dented edges associated with increased risk of partial delamination, a MAP suitable tray should have larger corner radii and reinforced areas like ribbing. This allows the package to collapse during the pressure ramp-up phase and to fully expand during the pressure release phase. Therefore, headspace volume, film and package design must be rigorously evaluated in order to prevent delamination, flex cracking, deformation and stresses to the packages. Figure 8.4 shows examples of suitable MAP products after a high pressure treatment at 600 MPa for 3 min.

Under high pressure, semicrystalline films like PA (colloquially known as nylon) show a decrease in permeability with increasing pressure. This effect is reversible and derives from the reduction of the polymer free volume under pressure [17–19]. However, during the pressure ramp-up phase of an HPP cycle, gases are absorbed within the film and food matrix



Figure 8.4 Package design examples for MAP and HPP (Source: Multivac).

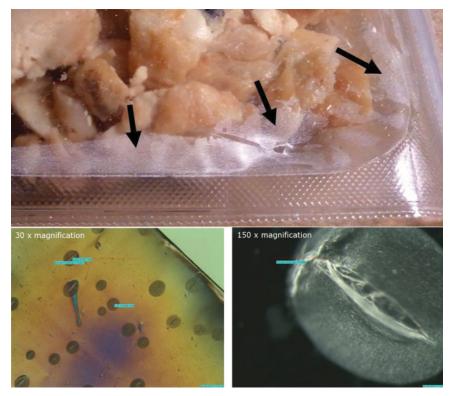
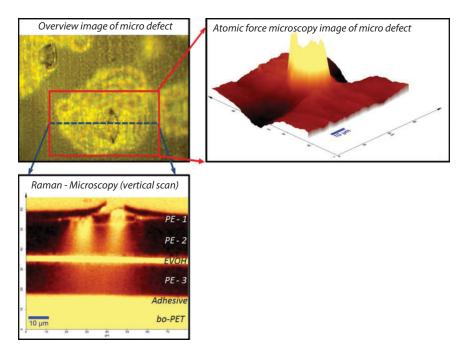


Figure 8.5 Typical micro defects / white spots (Source: Multivac).

[20]. This amount of gas absorbed can potentially create irreversible damage, microdefects and losses in permeability upon an uncontrolled quick release of pressure (see microdefects in Figure 8.5).

Packaging damages, including microdefects, are created due to the rapid volume expansion of gases, which are present within the film or food matrices while the pressure drops. One study showed that an extremely fast decompression rate (20,850 MPa/min) led to the formation of white opaque areas and lines on the surface of a PP/PEF film, especially when using increased headspace [21]. Figure 8.6 shows an example of the micro-defects created followed by Raman and atomic force microscopy. These kinds of microdefects could be overcome by controlling the decompression gradient and pattern of the high pressure profile [18]. Figure 8.7 shows the impact of an uncontrolled fast decompression in comparison with a controlled decompression on the film after HPP of a MAP product with 70%  $N_2/30\%$  CO<sub>2</sub> headspace at 600 MPa for 3 min.



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Figure 8.6 Raman microscopy showing impact of microdefects on film layers. [22]



**Figure 8.7** Effects of decompression rate on packaging: (a) microdefects (white-spots) after uuncontrolled, fast decompression; (b) intact product after HPP with a controlled decompression. MAP product with 70%  $N_2/30\%$  CO<sub>2</sub> headspace at 600 MPa, 3 min (Source: Multivac).

However, packaging material selection yet remains a challenge for certain laminate compositions. It is known that absorbed molecules within the amorphous areas of polymeric films can lead to morphologic changes. Absorbed gases like  $CO_2$  can lead to a decrease of the glass transition temperature, which would affect the brittleness of the film [23].

Modified atmosphere packaging in combination with HPP is currently being further developed as an alternative process and companies like Multivac are further exploring potential packaging able to endure such a process.

## 8.4 Active Packaging Materials for HPP

The application of active packaging materials containing antimicrobial agents holds some promise to further enhance the efficiency of HPP for food safety and shelf-life extension applications. There is evidence that antimicrobial packaging can have strong synergistic effects with HPP to control pathogens in meat products [24,25]. For example, combining HHP at 400 MPa and nisin- or lactate-containing interleavers successfully inhibited L. monocytogenes growth in ham slices for 30 days at 6°C, whereas the bacteria were able to grow in HPP batches without active packaging or non-HPP but actively packaged ham slices [24]. Another study investigated the antimicrobial properties of active PLA-based materials containing either carvacrol or allyl isothiocyanate (AITC) during storage and after HPP (up to 800 MPa at room temperature) [26]. The combination of active AITC-based films with HPP at 300 MPa was proven to be more efficient for inhibiting *B. cinerea* growth on a model food system than either HPP at 800 MPa or antimicrobial packaging used alone, even though the quantity of active compound released from the film was lower than the minimal quantity required to obtain inhibition at atmospheric pressure. Hence, this synergistic effect of HPP and antimicrobial agent can be used to reduce the quantity of active agents used in antimicrobial film and/or to reduce intensity of the HP treatment.

One limitation of cold HPP is that microbiological spores tend to be resistant to the treatment. Oxygen present in most food systems appears to reduce the bactericidal effect of HPP on spores. Thus, the combination of active oxygen-scavenging films with HPP to control bacterial and fungal spores in food systems has been explored [27]. OPET/EVOH/O<sub>2</sub>-scavenger/CPP multilayer laminate, using reducible organic compounds (e.g., quinones) as oxygen-scavenger material, were found to be effective inhibitors for *Neosartorya fischeri* spores in nutrient broth contained in

pouches when HPP at 600 MPa for 1 min was performed before storage at 30°C. Also, inactivation and inhibition of *Bacillus subtilis* spores in nutrient broth during storage at 30°C, was enhanced when HPP was performed. Results indicated that the enhanced reduction of spore growth obtained using the combination of oxygen scavenging and HPP can be achieved independently of the sequence in which these two steps are performed.

## 8.5 Challenges Encountered after HPP

High pressure processing can alter the integrity of multilayered materials, including the adhesion between layers. The adhesion between layers can be compromised if compressibility and resilience of individual layers differ significantly. The resulting gaps between the layers may even affect the microbiological safety of the package [9]. When an inelastic packaging material is used, severe deformation is expected to occur during the process [28].

Films with functional Al, AlOx, SiOx or other inorganic barrier layers provide less tensile strength and tend to delaminate more easily during HPP [14,29]. Polymer-based barrier layers like EVOH have material properties which are more akin to commonly used film layers such as PE, PP or PET. Therefore, these laminates may provide a more homogenous tensile strength and availability for a broader range of HPP applications. Therefore, depending on the package multilayer composition, both reversible and irreversible phenomena may occur in packaging materials exposed to HPP. These phenomena could be further distinguished between direct and indirect HPP-related effects [5].

Migration of packaging components into the food product after application for high pressure has been largely dismissed. For example, the global migration values of several multilayer packaging materials, including PET/ Al/PP and PE/EVOH/PE, into model foods were below the EU legislation limit (10 mg/dm<sup>2</sup>) after 30 min HPP at 200–500 MPa and 25°C [6]. Similarly, Mauricio-Iglesias *et al.* [30] reported that 5 min treatments at 800 MPa and 20 to 115°C and subsequent storage did not result in Uvitex OB and Irganox 1076 migration from synthetic common packaging (LLDPE) into four standard liquid food models. Similarly, migration of aroma compounds into PLA was reported minimal after 5 min HPP at 800 MPa and 40°C [31]. However, application of 800 MPa at 115°C notably increases the uptake of aroma compounds in the phase transition of the PLA material.

In the package system, compression forces not only act on the food materials, but also on the contained gas by compressing it almost completely [4]. Food materials are compressed similarly to water, resulting in limited volume reduction. Furthermore, compression forces act on the polymeric materials forming the package, reducing the overall volume of food package. Once pressure is released, the food package system undergoes a reversible or quasi-reversible return to its initial volume.

Pressurization of compressible substances, such as a food product, results in a temperature increase correlated to pressure increase. The extent of this temperature rise depends on the pressure, the temperature prior to pressurization, and the thermal and physical properties of the food and packaging. As well as foods, packaging materials undergo compression heating. For example, polymers like PP and PE undergo compression heating greater than water, as shown at low and high pre-pressurization temperatures and pressure up to 750 MPa [32]. In particular, the temperature increase with pressure is not linear; therefore, the relative increase with respect to water depends on the pressure range selected as well as the pre-pressurization temperature.

In a high-temperature/high-pressure process, the preheating step may influence the integrity of some tested packages in terms of oxygen permeability [7], particularly if temperatures higher than 85°C are utilized. Blistering and delamination has been observed in five packaging materials (PA/coextruded EVOH, PA/PP, PET/Al/CPP from two suppliers, and PA/Al/PP) that initially met the oxygen barrier criterion (0.06 ml/m<sup>2</sup>/ day) for long life shelf-stable products. None could survive the preheating stage, with an observed increase in oxygen permeability between 380 and 37,000%. However, the seal strength of Al-based pouches can be improved by preheating and subsequent application of high temperature pressurization due to the use of PP as the internal layer in the package.

Limited information has been reported in terms of the influence of other variables such as the film thickness, the type of food simulant contained, and the pressurization or depressurization rates before and after HPP on packaging integrity and migration properties.

## 8.6 Laminate Selection for HPP at Low Temperature

A literature review on packaging materials evaluated for conventional cold HPP has been published elsewhere [33]. Examples of laminate materials classified according to the main barrier component where applicable (i.e., EVOH, PVDC, PA, Al-based and metalized) are shown in Table 8.5. Another material commonly used in high-pressure, low-temperature applications [34] is LPDE.

**Table 8.5** Integrity, permeability and material properties of selected packaging materials for high pressure processing at low tem-

Test film structure	Thickness	Manufacturer	Max pressure	Physical/	Oxygen	Water	Tensile	Elongation	Elastic	Seal strength	Refs.
	(unt)		/time/ initial temp. (MPa/ min°C)	visual integrity (delamination)	permeability (control) % post HHP	permeability (control) % post HHP	strength (control c.d., MPa) % post	(control c.d., %) % post HHP	modulus (control c.d., MPa)	(control c.d. (N/15mm)) % post HHP	
			,		4		ЧНН		% post HHP	4	
EVOH-based											
LLDPE/EVA/EVOH/	n/a	Pira	400/30/60	retained	(0.74)-15%	(1.9)-5%	(27 N) +1%	(530.0)+0%	n/a	%0+(¿)	[4]
EVA/LLDPE											
LDPE/EVOH/LDPE/	500	Wipak	600/60/20	n/a	n/a	(0.92)0%	(70.1)+5%	n/a	n/a	(82.6)+0%	[10]
APET/Exp.											
PET/APET											
PE/PA/EVOH/PE	140	Wipak	600/60/20	n/a	n/a	(6.0)-5%	(58.3)+0%	n/a	n/a	(52.7)+8%	[10]
PE/nylon/EVOH/PE	62.5	Cryovac	800/20/45	retained	(~2) +2%	(~23) +1%	(20.4)-18%	(529.6)+2%	(344.4)+1%	n/a	[29]
PP/EVOH/PP	35/10/60	Nippon	600/10/20	retained	(4.8)+10%	(5.2)+15%	(3.3)-3%	n/a	n/a	(3.3)+3%	[37]
		Synthetic									
		Chemical									
		Industry									
PVDC-based											
PET/PVDC/nylon/ HDPF/PP	102.5	Rexam Inc	800/20/45	retained	(~2) +2%	(~3) +1 %	(66.5)+15%	(106.7)+0%	(558.0)+5%	n/a	[29]
PET/PVDC/PE free	(12/1/50)	Soplaril-Sodap	500/30/20	retained	(11)+10%	(3.5)+109%	(347.0)+8%	n/a	n/a	(3.5)+6%	[6]
radical, linear	65										
PA(nylon)-based											

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Test film structure	Thickness	Manufacturer	Max pressure	Physical/	Oxygen	Water	Tensile	Elongation	Elastic	Seal strength	Refs.
	(mn)		/time/ initial	visual integrity	permeability	permeability	strength	(control c.d.,	modulus	(control c.d.	
			temp. (MPa/	(delamination)	(control) %	(control) %	(control c.d.,	%) % post	(control	(N/15mm)) %	
			min°C)		post HHP	post HHP	MPa) % post	dHH	c.d., MPa)	post HHP	
							ЧНР		% post		
									ННР		
PA/PE free radical,	(30/60)100	Soplaril- Sodap	500/30/20	retained	(66)+2%	(5.9)-25%	(149.8)+32%	n/a	n/a	(3.8)-8%	[9]
linear											
PA/PE surlyn:ionomer	(40/55)	RC302 Soplaril-	500/30/20	retained	(62)-16%	(10.5)-47%	(192.2)+19%	n/a	n/a	(3.5)+4%	[9]
Zn	110	Sodap									
PA/ MDPE	(20/70)	Soplaril-Sodap	500/30/20	retained	(68)+26%	(3.5)+24%	(177.5)+16%	n/a	n/a	(2.6)-6%	[9]
	100										
PP/nylon/PP	115	Rexam Inc	800/20/45	retained	(~5)+~10%	(~5)+~2%	(57.2)-7%	(63)+8%	(457.5)+0%	n/a	[29]
PE/nylon/PE	50	Cryovac	800/20/45	retained	(~95) +5%	(~16) +2%	(23.3)+125%	(126.2)+6%	(364.0)-3%	n/a	[29]
PA/PP/PE free radical,	(30/10/60)	KL174 Soplaril-	500/30/20	retained	(103)+2%	(4.1)+15%	(187.1)-9%	n/a	n/a	(2.7)-9%	[9]
linear	110	Sodap									
Al-based or metalized											
PET/Al/CPP	9/12/1970	Nippon	600/10/20	retained	(0.3)0%	%0(0)	(5.0)-4%	n/a	n/a	(4.6)-7%	[37]
		Synthetic									
		Chemical									
		Industry									

The EVOH and PVDC-based packaging high pressure treated at initial temperature lower or equal to 60°C has been shown to retain visual and physical integrity, thus showing no signs of delamination. In general, oxygen and water permeability after HPP remained within the specified deviation limits (within 12% deviation according to industrial norms). Although several PA-based materials have been tested, little has been reported on their visual integrity after HPP. In general, the PA barrier provides higher oxygen permeability values than EVOH and PVDC (Table 8.5); however, the required oxygen permeability will depend on the product application. In addition, the barrier properties of the EVOH and PA materials are best when dry. PA is known for its high water uptake properties of up to 30%. This could lead to swelling of the PA-layer and an enhanced risk of delamination during HPP. In a PA/PE composite, delamination seems to be affected by the thickness of each layer [6] and oxygen permeability increases by more than 12% in some reported packages. Even though PA is used for its toughness rather than barrier properties in some structures, these structures may be unsuitable for HPP. High barrier grades of PVDC are more brittle than EVOH and nylons and may undergo stress fracturing when HPP treated. On the other hand, a few metal-foil materials such as PET/Al/CPP have been reported to survive the high-pressure, low-temperature process without significant delamination.

## 8.7 Laminate Selection for HPP at High Temperature

In contrast to the extensive number of materials evaluated for integrity after conventional HPP, very few studies have reported the integrity and barrier properties of individual and multilayered composite films after preheating and high-pressure/high-temperature processing. Some EVOH materials, a PA-based material, and Al-based/metalized pouches have achieved acceptable visual integrity and/or permeability after high pressure and high temperature, and their suitability will depend on the composition and high pressure/temperature conditions applied (Table 8.6).

Single-layer materials used in the food industry as water vapor transfer barriers, namely, PA, EVOH, PET, PP, and aluminum oxide coating, have been reported to survive high-pressure/high-temperature processing [7]. Most reports include visual integrity and oxygen permeability, however, little has been reported in terms of water permeability and strength properties.

Some EVOH-based materials were reported to retain visual integrity after high-pressure/high-temperature processing. White stains, due to

**Table 8.6** Integrity and permeability of selected packaging materials for high pressure processing at high temperatures (> 60°C before pressurization).

Detote pressui ization)							
Test film structure	Thickness (µm)	Manufacturer	Max pres- sure/time/ initial temp. (MPa/ min/°C)	Physical/ visual integ- rity (delami- nation)	Oxygen permeability (control) % post HHP	Water per- meability (control) % post HHP	Refs.
EVOH-based							
PA/EVOH/PE	75	Winpak (Deli*1)	690/10/95	retained	n/a	n/a	[14]
PP/EVOH26/	100/10/100	Nippon Synthetic	800/10/75	retained	(0.6)-2%	n/a	[16]
PPcoextruded (w adhesive)		Chemical Industry					
PP/EVOH48/PP	100/10/100	Nippon Synthetic	800/10/75	retained	(40.9)-7%	n/a	[16]
coextruded (w		Chemical					
auliesive)		A JISUDILI					
PA (nylon)-based							
PE/PA(nylon6)/PE	(28/45/27)100	Pliant Corp.	800/10/70	n/a	(15.2) + 15%	(5.5)+7%	[38]
		Schaumburg, Ill., USA					
Al-based or metalize	pa						
PA/Al/PP	n/a	The Pyramid	688/3/88	retained	(0.05) +780% (360.8)+75%	(360.8)+75%	[7]
		Group, La Habra,CA		(blisters)			

Test film structure	Thickness (µm)	Manufacturer	Max pres- sure/time/ initial temp. (MPa/ min/°C)	Physical/ visual integ- rity (delami- nation)	Oxygen permeability (control) % post HHP	Water per- meability (control) % post HHP	Refs.
PET/ON/ Al/R-CPP	12/15/7/70	n/a	600/5/95	delamination (<0.05) 0%	(<0.05) 0%	(<0.02) 0%	[20]
PET/Al/CPP Other	12/7/70	n/a	600/10/92	delamination (<0.05) 0%		(<0.02) 0%	[20]
PET/PE	n/a	Ampac Flexibles Corporation, Minneapolis, MN	688/3/88	retained	(78.2)-68%	n/a	[7]

partial delamination, have been seen in the coextruded PA/PP/EVOH/PP [35]. Ayvaz *et al.* [36] processed baby carrots in PA/EVOH/EVA at 600 MPa and 110°C for 10 min, seeing minimal impact in this high barrier packaging material after processing.

Aluminum-based pouches have shown effects from complete delamination to minor blistering as a result of high temperature. Bull *et al.* [20] reported a series of Al-based packages meeting the specifications for standard retort pouches after high-pressure/high-temperature processing. However, further research is needed to identify other suitable retort pouches for high pressure and high temperature. On the other hand, a study by Koutchma *et al.* [7] also reported that the magnitude of the increase in oxygen permeability in Al-based pouches (PET/Al and PA/Al/ PP) was significantly less than that observed in traditional thermal treatment (121°C for 3 min in steam retort).

## 8.8 Final Remarks

Design of primary, direct contact packaging for HPP requires consideration of the geometry and format to maximize loading efficiencies in cylindrical pressurization vessels, while providing attractiveness and added value to niche markets. Packages should be tailored for HPP by taking into account the overall HPP process control, type of product and packaging, package geometry and format, packaging films and film laminate structure, and type of barrier layer. A few materials utilizing PET, PE, PP, as well as PS-EVOH, PE-EVOH, and other metallic films are currently being utilized for commercial production. However, not all the specifications required to determine the suitability of such packaging for applications (i.e., visual integrity, gas permeability, seal and physical strength properties, and global migration of packaging components into the food) have been considered together in the scientific literature. At least one of these properties was not assessed for packages reported, not enabling a complete screening of packaging after HPP based on literature. Visual integrity failure by delamination or blistering is sufficient to discard the material for a given processing condition and in many publications integrity issues have not been fully addressed. In addition, the HPP conditions reported in the literature are variable due to differences in maximum pressure and temperature achievable by laboratory-scale HPP systems. Therefore, a standardized approach for packaging evaluation for HPP is required for future screening of multi-laminate materials.

In general, the literature indicates that EVOH-based materials show no deviations after conventional, low temperature (i.e., < 60°C) HPP in terms of visual integrity, permeability, and physical properties, making it a suitable packaging material for high barrier applications. Modified atmosphere packaging is an innovative, in many cases industrially proven, addition to HPP, particularly in the development of meat products or products that degrade easily in the presence of oxygen. The challenge is to overcome the potential delamination defects caused by the presence of gas in the package. However, newly selected materials and a comprehensive high-pressure process control are overcoming the problem.

For high-pressure/high-temperature processing, some EVOH- and PA-based materials, and a few Al-based/metalized materials, show potential for further developments. However, care must be taken to consider the effect of the preheating process on the overall integrity of the package. For packaging materials surviving the preheating process in terms of visual integrity, oxygen permeability changes observed between preheating and high pressure and high temperature were minor [7]. However, others have identified Al-based packages able to retain oxygen permeability but with-out much success in retaining packaging integrity under the harsh high-pressure/high-temperature conditions required for food sterilization [20].

Further research is required in the screening of new materials that are finding applications in thermal processing (hot fill or retort) for their potential use in HPP processes. The identification of transparent materials is desirable due to higher consumer preference. For example, thin vacuum deposited coatings of  $SiO_x$  on PET, PP or PA, that are transparent and water resistant, are appearing in retortable microwaveable options. Another option is the evaluation of new barrier polymers currently used as discrete layers with an oxygen permeability value 50 to 100 times lower than PET. There is a trend to use more plastic-based, stronger packaging materials that provide higher durability and meet the demand for higher line speeds and packaging waste reduction. Additionally, in active packaging like MAP, the use of antimicrobial films or films with natural volatile antimicrobial compounds adds to the hurdle concept of microbial control and provides an enormous potential for cold HPP applications.

#### References

1. Richter, T. Machine and method for the packaging and high pressure treatment of products. Patent DE102009042083B3, also published as EP2308759A3, US20110067355, 2011.

#### 278 FUNCTIONAL POLYMERS IN FOOD SCIENCE

- 2. Tonello-Samson, C. Packaging materials utilised in commercial applications. Personal Communication, 2012.
- 3. Caner, C., Hernandez, R. J., Harte, B. R. High-pressure processing effects on the mechanical, barrier and mass transfer properties of food packaging flexible structures: A critical review. *Packaging Technology Science* 17 (1): 23–9, 2004.
- 4. Mertens, B. Packaging aspects of high pressure food processing technology. *Packaging Technology Science* 6:31–36, 1993.
- Fleckenstein, B., Sterr, J., Langowski, H.-C. The effect of high pressure processing on the integrity of polymeric packaging: Analysis and categorization of occurring defects. *Packaging Technology Science*, doi: 10.1002/pts.2018, 2013.
- 6. Lambert, Y., Demazeau, G., Largeteau, A., Bouvier, J. M., Laborde-Croubit, S., Cabannes, M. Packaging for high-pressure treatments in the food industry. *Packaging Technology Science* 13 (2): 63–71, 2000.
- Koutchma, T., Song, Y., Setikaite, I., Juliano, P., Barbosa-Canovas, G. V., Dunne, C. P., Patazca, E. Packaging evaluation for high-pressure high-temperature sterilzaition of shelf-stable foods. *Journal of Food Process Engineering* 33 (6): 1097–114, 2010.
- 8. Venugopal, V. Retort pouch packaging. In *Seafood Processing: Adding Value through Quick Freezing, Retortable Packaging, Cook-Chilling and Other Methods*, pp. 197–215. CRC Press: New York, 2006.
- 9. Lange, J., and Wyser, Y. Recent innovations in barrier technologies for plastic packaging: A review. *Packaging Technology Science* 16 (4): 149–58, 2003.
- 10. Dobias, J., Voldrich, M., Marek, M., Chudackova, K. Changes of properties of polymer packaging films during high pressure treatment. *Journal of Food Engineering* 61:545–549, 2004.
- Caner, C., Harte, B. R. Effect of high-pressure processing on the migration of antioxidant Irganox 1076 from polypropylene film into a food simulant. *Journal of the Science of Food and Agriculture* 85:39–46, 2005.
- Li, W., Jian, P., Huiming, X., Yi, Y., Chunming, L. Inactivation of S. aureus and E. coli by the synergistic action of high hydrostatic pressure and dissolved CO<sub>2</sub>. *International Journal of Food Microbiology* 144:118–125, 2010.
- Park, S. J., Park, H. W., Park. J. Inactivation kinetics of food poisoning microorganisms by carbon dioxide and high hydrostatic pressure. *Journal of Food Science* 68 (3): 976–981, 2003.
- Schauwecker, A., Balasubramaniam, V. M., Sadler, G., Pascall, M. A., Adhikari, C. Influence of high-pressure processing on selected polymeric materials and on the migration of a pressure-transmitting fluid. *Packaging Technology Science* 15 (5): 255–62, 2002.
- 15. Götz, J., and Weisser, H. Permeation of aroma compounds through plastic films under high pressure: In-situ measuring method. *Innovative Food Science and Emerging Technology* 3 (1): 25–31, 2002.
- 16. Lopez-Rubio, A., Lagaron, J. M., Hernandez-Munoz, P., Almenar, E., Catala, R., Gavara, R., Pascall, M. A. Effect of high pressure treatments on the

properties of EVOH-based food packaging materials. *Innovative Food Science and Emerging Technologies* 6:51–58, 2005.

- 17. Richter, T., Sterr, J., Jost, V., Langowski, H. High pressure-induced structural effects in plastic packaging. *High Pressure Research* 30 (4): 555–66, 2010.
- 18. Richter, T. Method for high pressure processing of products. Patent EP 2308325B1, also published as DE102009042088A1, US20110070341, 2012.
- Schmerder, A., Richter, T., Langowski, H., Ludwig, H. Effect of high hydrostatic pressure on the barrier properties of polyamide-6 films. *Brazilian Journal of Medical and Biological Research* 38 (8): 1279–1283, 2005.
- Bull, M. K., Steele, R. J., Kelly, M., Olivier, S. A., Chapman, B. Packaging under pressure: Effects of high pressure, high temperature processing on the barrier properties of commonly available packaging materials. *Innovative Food Science and Emerging Technologies* 11 (4): 533–7, 2010.
- 21. Fairclough, J. P. A., and Conti, M. Influence of ultra-high pressure sterilization on the structure of polymer films. *Packaging Technology Science* 22 (5): 303–10, 2009.
- 22. Richter, T. Der Einfluss hohen hydrostatischen Drucks auf polymere thermoplastische Lebensmittelverpackungen. Dissertation Technische Universitaet Muenchen: 97, 2011.
- 23. Boyer, S. A. E., and Grolier, J. P. E. Modification of the glass transitions of polymers by high-pressure gas solubility. *Pure and Applied Chemistry* 77 (3): 593–603, 2005.
- 24. Jofre, A., Garriga, M., Aymerich, T. Inhibition of Listeria monocytogenes in cooked ham through active packaging with natural antimicrobials and high-pressure processing. *Journal of Food Protection* 70 (11): 2498–2502, 2007.
- 25. Jofre, A., Aymerich, T., Garriga, M. Assessment of the effectiveness of antimicrobial packaging combined with high pressure to control Salmonella spp in cooked ham. *Food Control* 19 (6): 634–638, 2008.
- 26. Raouche, S., Mauricio-Iglesias, M., Peyron, S., Guillard, V., Gontard, N. Combined effect of high pressure treatment and anti-microbial bio-sourced materials on microorganisms' growth in model food during storage. *Innovative Food Science and Emerging Technologies* 12 (4): 426–434, 2011.
- 27. Scully, A., Zerdin, K., Rooney, M., Hocking, A., Stewart, C. Inactivation of microbiological spore comprises absorbing oxygen from environment about the spore to limit the consumption of oxygen by the spore. Patent WO2005041694-A1, 2005.
- 28. Guillard, V., Iglesias, M., Gontard, N. Effect of novel food processing methods on packaging: Structure, composition, and migration properties. *Critical Reviews in Food Science and Nutrition* 50 (10): 969–88, 2010.
- 29. Caner, C., Hernandez, R. J., Harte, B. R. High-pressure processing effects on the mechanical, barrier and mass transfer properties of food packaging flexible structures: A critical review. *Packaging Technology Science* 17 (1): 23–9, 2004.

#### 280 FUNCTIONAL POLYMERS IN FOOD SCIENCE

- Mauricio-Iglesias, M., Jansana, S., Peyron, S., Gontard, N., Guillard, V. Effect of high-pressure/temperature (HP/T) treatments of in-package food on additive migration from conventional and bio-sourced materials. *Food Additives and Contaminants Part a-Chemistry Analysis Control Exposure and Risk Assessment* 27 (1): 118–127, 2010.
- Mauricio-Iglesias, M., Peyron, S., Chalier, P., Gontard, N. Scalping of four aroma compounds by one common (LDPE) and one biosourced (PLA) packaging materials during high pressure treatments. *Journal of Food Engineering* 102 (1): 9–15, 2011.
- Knoerzer, K., Buckow, R., Versteeg, C. Adiabatic compression heating coefficients for high pressure processing: A study of some insulating polymer materials. *Journal of Food Engineering* 98 (1): 110–119, 2010.
- Juliano, P., Koutchma, T., Sui, Q., Barbosa-Canovas, G. V., Sadler, G. Polymericbased food packaging for high pressure processing. *Food Engineering Reviews* 2 (4): 274–297, 2010.
- Le-Bail, A., Hamadami, N., Bahuaud, S. Effect of high-pressure processing on the mechanical and barrier properties of selected packaging. *Packaging Technology Science* 19 (4): 237–43, 2006.
- Moueffak, H. E., Cruz, C., Demazeau, G., Montury, M. Effects of high pressure on packaging materials for food stabilisation. In *High Pressure Research in the Bioscience and Biotechnology*, ed. K. Heremans, pp. 467–470. Leuven University Press: Leuven, 1997.
- Ayvaz, H., Schirmer, S., Parulekar, Y., Balasubramaniam, V. M., Somerville, J. A., Daryaei, H. Influence of selected packaging materials on some quality aspects of pressure-assisted thermally processed carrots during storage. *LWT-Food Science and Technology* 46 (2): 437–447, 2012.
- Masuda, M., Saito, Y., Iwanami, T., Hirai, Y. Effects of hydrostatic pressure on packaging materials for food. In *High Pressure and Biotechnology*, eds. C. Balny, R. Hayashi, K. Heremans, P. Masson, pp. 545–547. John Libbey Eurotext: London, 1992.
- Halim, L., Pascall, M. A., Lee, J., Finnigan, B. Effect of pasteurization, highpressure processing, and retorting on the barrier properties of nylon 6, nylon 6/ethylene vinyl alcohol, and nylon 6/nanocomposites films. *Journal of Food Science*, 74:N9–N15, 2009.

# Inorganic-Organic Hybrid Polymers for Food Packaging

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#### Abstract

The use of polymer materials in food packaging is one of the fastest growing global trends. There has been serious interest and effort over the last few years in the advancement of novel food packaging concepts which can play a proactive role in food preservation and shelf life extension. Homogeneous blending of inorganic and organic moieties in a single-phase material offers extraordinary opportunities to tailor barrier, mechanical, antimicrobial and other properties with respect to food packaging application. Numerous hybrid inorganic-organic materials have been developed using low temperature sol-gel chemistry, which enables the tailoring of the nanostructure and the resulting material is often multifunctional, offering a wide range of interesting properties. These new materials can be effectively used as transparent barrier coatings to obtain high-barrier properties for oxygen, water vapor, and flavor permeation. Active oxygen barrier layers and nanosensors based on inorganic-organic hybrids can also be produced via the sol-gel method, particularly for advanced food packaging. In recent years, nanocomposites, where polymers are formulated with fillers of nanometric dimensions, have become a rapidly emerging field due to their huge potential to improve the performance of materials in polymer packages. Due to the nanometer size dispersion of the filler particles, these composites, especially natural polymer-layered silicate nanocomposites, exhibit markedly improved properties such as increased modulus and strength, decreased barrier properties, increased thermal stability, etc. Polymer nanocomposites-based packaging materials can also serve as carriers of some active substances and nanosensors for tracing and monitoring the condition of

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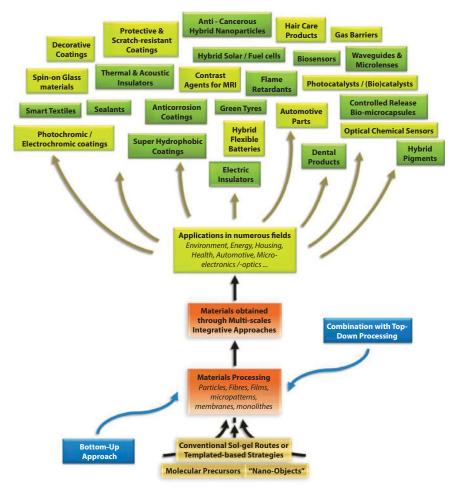
food during transport and storage. This chapter gives a brief overview of developments in hybrid inorganic-organic polymers and nanocomposites for food packaging application.

*Keywords:* Inorganic-organic hybrid polymers, sol-gel synthesis, polymer nanocomposites, properties, food packaging

## 9.1 Introduction

Hybrid inorganic-organic materials can be broadly defined as composites with intimately mixed organic and inorganic building blocks [1,2]. These are promising systems for a variety of applications due to their extraordinary properties, which arise from the synergism between the properties typical of each of the constituents [3]. By combining different kinds of inorganic and organic components and varying their proportions at the molecular level, hybrid materials with superior properties (mechanical, thermal, chemical, optical, barrier, etc.) compared to their pure counterparts can be generated [4]. This again, makes it possible to fine-tune material properties and design systems for specific applications. The seemingly unlimited variety, unique structure-property control, and the compositional and shaping flexibility give these materials a high potential [5]. Another motivational force is the possibility to create multifunctional materials. Unlike the pure inorganic materials which often require high temperature treatment, these materials show more polymer-like handling because of their large organic content or due to crosslinked inorganic networks which makes the processing of these materials very simple [3]. Hence, hybrid materials can be processed to any form such as gels, monoliths, thin films, fibers, particles or powders. Consequently, inorganic-organic hybrid materials are considered to be treasured for application in numerous areas, for example in optics, catalysis, sensor technology, electronics, magnetism, mechanics, and food and beverage packaging [6]. The increasing impact of hybrid materials is summarized in Figure 9.1.

Successful commercial inorganic-organic hybrid polymers have been part of manufacturing technology since the 1950s and have emerged with the development of the polymer industry [6,7]. However, the field of inorganic-organic hybrid materials has grown rapidly since the 1980s with the expansion of soft inorganic synthetic processes and availability of novel physicochemical characterization methods [8,9]. In particular, the mild synthetic conditions offered by the sol-gel process (metallo-organic precursors, organic solvents, low processing temperature, and processability



**Figure 9.1** Impact of hybrid materials in academic and industrial sectors (reproduced with permission from [1]).

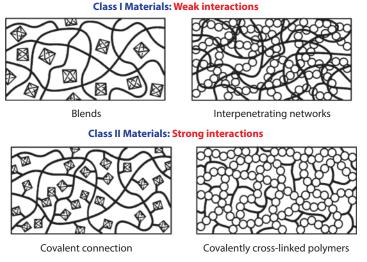
of the colloidal state) was one of the major driving forces for the development of the so-called functional hybrid materials [6].

Generally, hybrid materials are constituted of organic polymers and inorganic components, mainly metal oxide and metal-oxo polymers or others such as phosphates, carbonates and chalcogenides [1]. The inorganic part is generally amorphous networks, nanocrystalline networks or metal-oxo clusters which are formed via condensation of metal organic precursors or metallic salts. The size of the inorganic component can vary from lower micrometer to nanometer range. The term "nanocomposite" is used if the discrete inorganic structural units have dimensions in the nanometer length scale (1–100 nm) and the term "hybrid materials" is more often used if the inorganic units are formed *in situ* by molecular precursors [9].

## 9.2 Classification and Terminology of Inorganic-Organic Hybrids

### 9.2.1 Classification Based on Type of Interaction

Inorganic-organic hybrid materials are not simply physical mixtures but also have a high level of mixing of inorganic and organic components at the nanometer or molecular level [10]. Such materials can be either a homogeneous mixture derived from monomers and miscible or compatible organic/inorganic components or heterogeneous mixture (phaseseparated system or nanocomposite), where one of the domains has a dimension ranging from a few angstroms to several nanometers [11–13]. A distinct characteristic of hybrid materials is that their properties are related not only to the chemical nature of individual components but also to the nature of interface between them [14]. Hence, based on the nature of interaction at the interface, these materials are categorized into two distinct classes: Class I materials with weak bonds (hydrogen, van der Waals or ionic) and Class II materials with strong bonds (covalent, coordination, iono-covalent) [15,16]. Examples of Class I materials include blends and interpenetrating networks. In blends, a weak crosslinking occurs by the entrapped inorganic units through physical interaction with the polymer matrix [4], while in the latter, the organic and inorganic network interpenetrate without strong chemical interactions [9]. Class II hybrids are formed when inorganic building blocks are covalently bonded to the organic polymers [9]. A critical challenge in the design of these Class II inorganicorganic systems is the control of the mixing between the two dissimilar phases. The preparation of these materials hence usually requires some effort to establish the chemical link (e.g., development of special precursors) between the organic and inorganic components to overcome the phase separation or leaching problems [4]. A pictorial representation of different types of hybrid materials is given in Figure 9.2.



**Figure 9.2** Types of inorganic-organic hybrid materials (reproduced with permission from [3]).

## 9.2.2 Classification Based on Morphological Combination

Another classification of inorganic-organic hybrid materials is based on the morphological combinations of the components [17] as follows: Class 1 – Inorganic matrix systems; where organic materials were embedded in an inorganic polymer. Class 2 – Organic matrix systems; where inorganic materials are embedded in an organic polymer. Class 3 – Interpenetrated networks systems; where inorganic and organic polymeric networks are independently formed without mutual chemical bonds. Class 4 – Truly hybrids systems; where inorganic and organic polymeric systems with mutual chemical bonds are formed. Class 5 – Inorganic core/shell matrix systems; where core/shell nanoparticles are in organic polymer structures.

## 9.2.3 Polymer Nanocomposites

While most compounds can be reasonably considered to be formed by a predominant matrix (be it organic or inorganic) and a host component inserted within the structure of the former, that is not the case for certain types of hybrids. These materials, formed by colloidal nanometer-sized particles (size  $\leq 100$  nm) of metals or metallic compounds in polymer matrix constitute a separate category called "polymer nanocomposites." In these materials, inorganic nanoparticles are not the host for the intercalation of organic polymers, but at the same time they are too large to

be considered guest species conforming to the structure of the polymers. These materials could therefore be considered as true composite materials where each component still retains its own structure but with an increased interfacial interaction derived from the particle size in the nanometer range [18]. Depending on the nature and surface functionality of the nanofillers, nanocomposites could exhibit modifications in their properties such as improved mechanical and barrier properties, higher transparency [19-22], etc. Such property enhancements rely on their nanoscale dispersion, even with a very low level of nanofiller incorporation ( $\leq 5 \text{ wt\%}$ ), which results in high aspect ratio and high surface area. The reinforcement efficiency of nanocomposites can match that of conventional composites with 40-50% of loading with classical fillers [19]. The different nanofillers can be classified depending on their aspect ratio and geometry, such as (i) platelet or layered particles (e.g., clay, graphene), (ii) spherical (e.g., silica or metal nanoparticles) or (iii) acicular or fibrous ones (e.g., whiskers, carbon nanotubes) [23]. Besides reinforcing nanoparticles, whose main role is to improve mechanical and barrier properties of the polymer materials, there are several types of nanostructures responsible for other functions, sometimes providing active or "smart" properties to the polymer system such as antimicrobial activity, enzyme immobilization, biosensing, etc. Some particles can have multiple applications, and sometimes the applications can overlap, such as some immobilized enzymes which can act as antimicrobial components, oxygen scavengers and/or biosensors [24].

## 9.2.4 Terminology

Depending on the process to make the inorganic-organic hybrids, they are associated with different names. The most versatile technique for the preparation of hybrid materials is the sol-gel process, where the formation of inorganic moieties starts from molecular precursors [4]. The hybrids made by the process where a silane coupling agent is used to modify the metal alkoxide, which is subsequently blended with reactive monomers and suitable catalysts for secondary polymerization to form a network, are called ORMOSILs (organically modified silanes) [25]. These materials are also known as ORMOCERs [26] to reflect their more ceramic-like properties following thermal treatment. These materials offer several advantages such as crack resistance, low light scattering, better mechanical properties, and flexibility [27].

Another class of inorganic-organic hybrid materials are CERAMERs [28], in which monolithic networks are prepared from reactive components

such as soluble metal alkoxides and an oligomer or polymer with alkoxysilane functionality. The brittleness and optical properties of the ceramics in these materials could be modified by appropriately choosing the polymeric species [29].

NANOMERs are surface modified or unmodified nanometer-scale materials available as fillers for a range of polymer resins from commodity polyolefins to specialty polyamides. Nano-effects have been demonstrated for resins in which nanomers are added either during polymerization or by melt-compounding [30]. These inorganic materials can impart properties such as wettability, coloration, selective adsorption, porosity, etc., to the resulting polymer nanocomposite or nanohybrids.

## 9.3 General Preparation Strategies for Organic-Inorganic Hybrid Polymers

There are a number of synthetic strategies to produce inorganic-organic hybrid materials in which the control of mixing the inorganic and organic phases differs, resulting in various degrees of homogeneity between the phases [31]. If the two phases have opposite properties or polarity, the system would thermodynamically phase-separate. The same can happen on the molecular or nanometer level leading to microphase separation [3]. This phenomenon in turn is related to the chemical nature of the interface developed during the synthesis processes [1]. The type of properties and additional functionalities required in the final materials also play a major role in choosing the synthesis route of these hybrids.

## 9.3.1 Class I Hybrids

In Class I materials, the lack of strong interaction between the inorganic and organic entities leaves some potential for dynamic phenomena in the final material, which may lead to particle aggregation or separation of discrete phases resulting in poor mechanical, optical, electrical, etc., properties [3]. Weak interaction becomes advantageous when mobility of one component in the other is required for targeted properties [9]. Otherwise these problems can be avoided by adopting proper synthesis strategies.

Class I hybrids are generally synthesized based on a bottom-up approach (Lego-like chemistry), where nanosized building blocks (BBs) self-assemble into dense or porous structures [32]. The BBs are often inorganic moieties (metal clusters, nanoclay minerals, nanoparticles, preformed colloidal

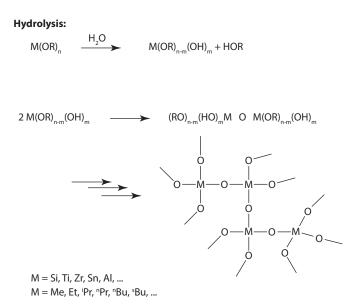
particles, etc.) with well-defined size, shape, tailored surface structure and composition [9]. The BBs may then be assembled in the second phase through intercalation chemistry, amphiphilicity driven self-assembly or electrostatic interactions [33]. The interface between two phases can be tailored by adding functional groups to the surface of the inorganic building blocks either by their post-synthesis modification (two-step process) or during their synthesis (*in situ*). The attachment of functional groups to the surface of the inorganic component occurs through different interaction mechanisms and hence a variety of organic groups can be applied for the functionalization process [9]. Similarly other methods employed to overcome the interface include use of polymers with functional groups that can interact with the modified surface of inorganic surfaces via formation of covalent bonds [25].

Generally, for the mixing of organic components with the inorganic part, three methods are used: (i) intercalation of monomers followed by *insitu* polymerization, (ii) direct intercalation of polymer chains from solution, and (iii) polymer melt intercalation. The incorporation of unmodified NBBs is done either by attaching an inert organic layer on the surface of the particle core (core shell) that can act as the compatibilizer at the particle/polymer interface, or by encapsulation of particles by special polymerization techniques such as emulsion polymerization [3].

Class I materials can also be synthesized by stimulating a phase separation by changes in the reaction conditions (e.g., temperature, pH), solvent composition, and polymerization process. In this method, the initially miscible system of the organic and inorganic constituents separates into structured domains. These hybrids can be later converted to porous structures either by calcination or by solvent extraction [19]. Another popular method of forming Class I hybrids is through templating (coating, casting or mineralization) of organic polymer [20]. This method is specifically used for producing macroporous and hierarchically structured materials.

### 9.3.2 Class II Hybrids

The most versatile method for the preparation of Class II hybrids is sol-gel processing, which allows the formation of inorganic entities starting from molecular precursors [4]. This process is basically an organic polycondensation reaction, which involves the successive hydrolysis and condensation of organically functionalized metal precursors to form crosslinked



Scheme 9.1 Sol-gel process (reproduced with permission from [3]).

3D-networks with metal-oxo (M-O) or metal-hydroxo (M-OH) bridges [34,35]. The reactions are presented in Scheme 9.1.

The inorganic precursors used are metal halides, metal or silicon alkoxides, and organometallic coordination compounds. The mild reaction conditions and the broad solvent compatibility offer the possibility to carry out this network-forming process with preformed organic polymer or to carry out the organic polymerization during or after the sol-gel process [9]. The type of solvent, catalyst and inorganic precursors along with their ratio determines the morphologies and properties of the sol-gel products [36]. The most prominent inorganic material formed during the sol-gel method is unmodified or organically modified SiO<sub>2</sub> using precursors Si (OR)<sub>4</sub> or  $R'_nSi$  (OR)<sub>4-n</sub> respectively. This process can be extended to other metal oxide precursors of Sn, Zr, Ce, Al, etc. Since C-Si bond is stable to hydrolysis, a variety of modifications can be directly incorporated to SiO<sub>2</sub> network, whereas for the organic modification of metal-containing inorganic moieties, coordination of multidentate ligands, which show a higher stability towards substitution reaction, is used [37].

The common methods used to incorporate an inorganic part to organic polymers applying the sol-gel approach are:

a) Mixing of the precursor for the sol-gel process with the preformed organic polymer followed by an inorganic

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polycondensation reaction. The structure of the preformed organic building block is retained in the final material. Organic polymers with functional groups which have specific interaction (e.g., hydrogen bonding) with the sol-gel compounds have to be selected for this strategy to avoid macrophase separation [3,38]. Parameters employed for solgel (e.g., pH, reaction time, temperature, solvent) have a crucial influence on the morphology of the inorganic species in the resulting material and its properties [39].

- b) Polymerization of an organic monomer in the inorganic gel. Here, the preformed inorganic structures are crosslinked by *in-situ* polymerization reactions or infiltration of the monomers [40]. To improve the interaction between inorganic and organic phases, coupling agents such as trialkoxy silanes with organic functionality (e.g., methacryloxytrimethoxy silane) are used [41].
- c) Simultaneous formation of the inorganic and organic network by the adjustment of hydrolysis conditions, making the reaction faster; hence phase separation can be minimized in this case [3].
- d) Dual network materials in which the molecular precursors for the formation of the two networks are covalently linked to each other, where bifunctional molecular precursors bearing an inorganic and an organic functionality [42] are used. The latter must be capable of undergoing polymerization or crosslinking reactions. Usually, these precursors are reacted first with water. After the formation of the inorganic network, the organic groups are polymerized or crosslinked to form extended organic structures.

The amount of incorporated inorganic moiety can be varied over a wide range. In addition to the sol-gel processing parameters, the morphology of the hybrid materials obtained by the interpenetration of polymers and inorganic moieties is dependent on polymer variables such as the molecular weight, the presence and extent of polymer functionality and shape, and the solubility of the polymer in the sol solution. Therefore, possibilities for synthesizing this type of materials are immense [3]. These strategies are simple, cost effective and produce amorphous nanocomposite hybrid materials exhibiting a variety of microstructures which can be transparent and easily shaped as films or bulks. The materials thus formed are cheap, very versatile, present many interesting properties and consequently give rise to many commercial products [1].

#### 9.3.3 Polymer Nanocomposites

The most traditional and easy method for the synthesis of inorganicorganic polymer nanocomposites is direct mixing of the nanoparticles into the polymer. The blending can generally be done by melt or solution mixing. The main difficulty in the mixing process is accomplishing an effective dispersion of the nanoparticles in the polymer matrix because they have a strong tendency to form agglomerates. In melt processing, particles are dispersed into a polymer melt and polymer inorganic nanocomposites are then obtained by extrusion. Solution blending is a liquid-state powder processing method that provides a good level of molecular mixing and is widely used in material preparation and processing. Some of the limitations of melt mixing can be overcome if both the polymer and the nanoparticles are dissolved or dispersed in solution, but there is a cost subject to the solvent and its recovery [43].

Another simple and efficient method to incorporate inorganic nanoparticles into polymers consists of performing *in-situ* growth inside the polymer matrix [44–47]. In this method, the particles are formed from their respective precursors in the presence of the polymer matrix. The incorporation of precursors into the polymeric matrix is usually achieved either from the gas or liquid phases, but it is also possible to mix the components in the solid phase. This step is followed by the removal of unwanted chemical products after the nanoparticles have formed. A number of pathways including chemical reductions, photo-reductions, and thermal decompositions can be used for the *in-situ* fabrication of nanoparticles [48,49].

An alternative approach consists of the concurrent formation of both the polymeric matrix and the nanoparticles, and it is considered to be a promising methodology for the synthesis of polymer nanocomposites. In this approach, precursors of the nanoparticles are dispersed into polymerizable monomers, and the polymer matrix is prepared simultaneously during the generation of the nanoparticles. Hence, the *in-situ* metal surfaces that are formed can catalyze or initiate the polymerization through a transfer of electrons from the metal surface atoms to the monomers. Thus, the degree of dispersion of the inorganic components may influence the formation of the nanoparticles, which in turn affects the degree and rate of polymerization achieved by the polymeric matrix [50].

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The sol-gel processing of nanoparticles inside of a polymer dissolved in nonaqueous or aqueous solutions results in the generation of interpenetrating networks between inorganic and organic moieties at low temperatures; this network improves the compatibility between components and builds strong interfacial interaction between the two phases. This process has been used successfully to prepare nanocomposites with silica, alumina, calcium oxide, and titania in an extensive range of polymer matrices [51].

## 9.4 Characteristics of Polymer-Based Food Packaging Materials

Over the last decades, the use of polymers as food packaging materials has increased massively due to their benefits over other traditional materials such as glass or metals [52,53]. A great benefit of polymers is the large diversity of materials and compositions available, which make it possible to adopt the most convenient packaging design to the very specific needs of each product. Characteristics of polymers such as their low cost, lightweight nature, thermosealability, ease of printing, microwaveability and optical transparency can also be adapted to specific requirements of the products. They can also be conformed into an infinite variety of sizes and shapes depending on the thermal and mechanical properties. Furthermore, polymers can also be incorporated in integrated production processes where the package is formed, filled and sealed in the same production line, making the process quick and cheap and avoiding the transport and storage of empty packages. Another important factor is that plastics can be selected with adequate chemical inertness to suit almost every food product [54,55].

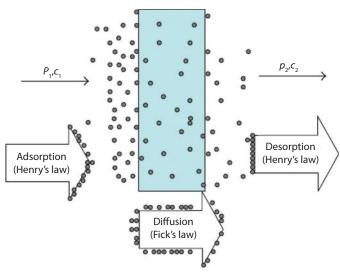
An important function of packaging, when regarded as a food preservation technology, is to retard food product deterioration, extending shelf life, and to maintain and increase the quality and safety of the packaged foods. Thus packaging materials provide physical protection and create appropriate physicochemical conditions for products that are necessary for obtaining a suitable shelf life. The packaging system, based on a proper choice of the packaging materials in conjunction with appropriate gas (e.g.,  $O_2$ ,  $CO_2$ ), light and water vapor barrier and mechanical properties, prevents product deterioration due to physicochemical or biological factors and maintains the overall quality during storage and handling [56]. Traditionally, food packages have been defined as passive barriers to delay the adverse effect of the environment on the contained product. However, the current tendencies include the development of packaging materials that interact with the environment and with the food, playing an active role in preservation. These new food packaging systems have been developed as a response to trends in consumer preferences toward mildly preserved, fresh, tasty, and convenient food products with a prolonged shelf life [57].

The use of different polymers in the food packaging industry depends on the properties of the food product. Also, manufacturing, handling, and packaging engineering procedures can influence the final properties of packaging material, especially in terms of barrier properties which are, further, strictly correlated to the intrinsic structure of the polymer such as degree of crystallinity, crystalline/amorphous phase ratio, nature of polymer, thermal and mechanical treatment before and after food contact, chemical groups present in the polymer (polar or not), degree of crosslinking, and glass transition temperature [58]. The selection of the best packaging material is a crucial point for the food market, because it needs to be versatile enough to withstand handling process forces maintaining physical and chemical integrity and suitable for barrier properties to several gases used in modified atmosphere packaging (MAP) techniques (e.g.,  $O_2$ ,  $N_2$ ,  $CO_2$ ) [3]. Furthermore, the intrinsic composition of the packed food (e.g., pH, fat content, aroma compound) may have influence on the sorption characteristics of the packaging materials, while environmental factors like temperature and, for some polymers, relative humidity, may affect their barrier characteristics [59].

#### 9.4.1 Permeability Behavior

Long-term preservation of food products requires packaging with high diffusion-barrier performance materials [60]. In contrast to glass or metal packaging materials, packages made with plastic are permeable at different degrees to small molecules like gases, water vapor, and organic vapor and to other low molecular weight compounds like aromas, flavors, and additives present in food. As a consequence of different barrier properties of the material, the transfer of these molecules ranges from high to low [61].

Permeability is generally defined as the quantification of permeant transmission, gas or vapor, through a resisting material [62,63]. So the concept of permeation is directly associated with barrier properties of polymer-based packaging materials. A permeant molecule moves through a barrier in a multistep process: the permeant dissolves in the film matrix at the higher concentration side, diffuses through the film driven by a concentration gradient, and desorbs from the other surface [61] (Figure 9.3).



Gas or vapour molecules

**Figure 9.3** General mechanism of gas permeation through plastic films (reproduced with permission from [61]).

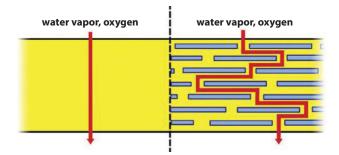
In virtually every case, the permeation is controlled by the dissolution and diffusion steps. The diffusion coefficient, D, is a measure of the speed of molecules moving in the polymer. The solubility coefficient, S, is an indication of the number of permeant molecules that are diffusing [64,65]. Based on Henry's law of solubility [66], Fick's law of diffusion [67], and assuming steady-state transport, the relationship between D, S and the permeation coefficient (P commonly called permeability) simplifies to:

$$P = D \times S \tag{9.1}$$

A low permeability may result from a low diffusion coefficient or a low solubility coefficient or both. The most commonly used SI unit (at STP) is  $cm^3/cm^2$  sec (cm Hg). When the permeability coefficient is measured with the manometric method,  $cm^3/m^2$  day bar is used to express the permeability value [61]. Several reports on conversion factors, gas transmission rate, are available in the literature [68–70].

Water vapor and oxygen are two of the main permeants studied in packaging applications, because they may transfer from the internal or external environment through the polymer package wall, resulting in a continuous change in product quality and shelf life [71]. The oxygen transmission rate of packaging materials is of great importance because oxygen promotes a lot of degradation mechanisms of a food, such as corrosive phenomena, oxidations, and great modification of organoleptic properties [72]. The water vapor barrier properties for the packaged product, whose physical or chemical deterioration is related to its equilibrium moisture content, are of great importance for maintaining or extending its shelf life. Water vapor transmission rate (WVTR) is mostly reported at standard conditions of temperature (37.8°C) and relative humidity (90%). Carbon dioxide has also become very important for MAP technology because it can potentially reduce the degradation phenomena associated with processed fresh vegetable products, leading to a significantly longer shelf life [73]. Generally, the permeabilities of  $N_2$ ,  $O_2$ , and  $CO_2$  are in the ratio 1:4:14. In addition to functioning as gas and moisture barriers, polymers are also utilized in packaging applications that require flavor, aroma, or solvent barriers [74].

Humidity and temperature can affect permeability of polymer films. When a polymer equilibrates with a humid environment, it absorbs water which may increase the permeability, whereas the permeability in general increases with increasing temperature. Additives can also play an important role in altering the permeation behavior of polymers. When a polymer is plasticized with small molecules that are soluble in polymer, it can increase the D of the permeant without affecting S. For inorganic fillers, the permeability might increase if the polymer does not wet the filler. The permeability will decrease if the polymer wets the filler. Filler in the form of platelets can lower the permeability when compared to filler with a more compact shape. If the platelets tend to lie in the plane of the film, permeant molecules must make wide detours (tortuous path) while traversing the film (Figure 9.4). This gives a greatly reduced effective diffusion coefficient [75].



**Figure 9.4** Illustration of the "tortuous pathway" created by fillers with platelet structure (a) diffusing gas molecules on average migrate via a pathway that is perpendicular to the film orientation; (b) diffusing molecules must navigate around impenetrable particles/ platelets and through interfacial zones which have different permeability characteristics than those of the virgin polymer (reproduced with permission from [75]).

Other factors such as size, shape, and polarity of the penetrating molecule of the permeant and crystallinity, degree of crosslinking and polymer chain are also influences on the permeation process. Since gas molecules cannot permeate through crystallites, an increase in crystallinity of a polymer can reduce the rate of gas transmission. Thus, the gas permeation into semicrystalline polymers is limited to the amorphous regions [61].

### 9.4.2 Mechanical Properties

The role of packaging material is to protect the original quality of foodstuff from undesirable external influences. Structural characteristics as well as conditions in which external forces take effect are crucial factors that influence increase in defects, random breaking and crevices in the material [76]. It is well accepted that the polymer design plays an important role in the mechanical properties, and consequently in the process utilized to model the final product (injection molding, sheet extrusion, blow molding, thermoforming, and film forming). In addition, many packages are commercially used below room temperature, so it is important to assess the mechanical performance of materials under these conditions [77]. The benefit of using polymers as packaging materials is the feasibility of tailoring a structure and mechanical properties to meet the requirement of protection, preservation and distribution of specific products. Mechanical properties of packaging materials include tensile strength, elongation, burst strength, tearing resistance and stiffness [78].

No pristine polymer exhibits all desired mechanical properties required for every conceivable food packaging application. Hence several hybrids have been developed by adding reinforcing fillers such as inorganic fibers, platelets, and particles to polymers to enhance their properties [79]. Mechanical properties of these filled polymers are affected by the shape, size, and orientation of the fillers [56]. Moreover, the dispersion and chemical nature of the filler also play a fundamental role in the mechanical properties of the hybrid materials [80]. Recent developments showed that polymer nanocomposites consisting of a polymer and nanometric inclusions exhibit remarkably improved mechanical and physical properties when compared to those of neat polymers. A uniform dispersion of nanoparticles leads to a very large matrix/filler interfacial area, which changes the molecular mobility, the relaxation behavior and the consequent thermal and mechanical properties of the material. Fillers with a high aspect ratio are particularly interesting because of their high specific surface area, providing better reinforcing effects [81-83]. Additionally,

optimizing the interfacial bond between the particle and the matrix, one can tailor the properties of the overall composite, similar to what is done in macrocomposites. For example, good adhesion at the interface will result in improved properties such as higher modulus, increased strength and heat resistance, higher shear strength, delamination resistance and corrosion resistance [84].

Tensile test analyses are made to determine the tensile strength (MPa), the percent elongation at yield (%), the percent elongation at break (%) and the elastic modulus (GPa) of the food polymer packaging material [73]. These values are important to get mechanical information of the materials to be compared with the commercial ones [85]. An impact properties test is a method utilized to determine the energy that causes the plastic to fail under specific impact conditions [86].

### 9.4.3 Other Properties

The interaction and absorption between chemical compounds and polymer may affect the final mechanical properties of a polymer. Normally the chemical resistance is tested measuring the tensile stress, elongation at break and modulus of elasticity of sample submerged in weak and strong acid solutions as a function of time, simulating real conditions, at ambient temperature (23°C), 18°C and 29°C. The weak acid solution is prepared with acetic acid while the strong acid solution is prepared with hydrochloric acid [77].

Good optical properties, such as high surface shine and transparency, are important for packaging materials to satisfy consumer demand for a clear view of the product. Traditional hybrid materials tend to be largely opaque because of light scattering by the particles or fibers embedded within the continuous phase. However in nanocomposites, the domain sizes are reduced to a level such that true "molecular composites" are formed [56]. Based on the molecular or nanoscale dimensions of the building blocks, light scattering in homogeneous hybrid material can be avoided, and therefore the optical transparency of the resulting hybrid materials and nanocomposites is relatively high [3].

Condensation (fogging) of water vapor on the inner surface of food packs can occur when the temperature of the pack environment is reduced, resulting in a temperature differential between the pack contents and the packaging material. Fogging of the inner surface of lidding film is a result of light scattering by the small droplets of condensed moisture that leads to poor product visibility and an aesthetically unpleasing appearance of the pack. This can be overcome by applying antifogging agents to the plastic heat-sealing layer, either as an internal additive or as an external coating. These chemicals decrease the surface energy of the packaging film, which enables moisture to spread as a thin film across the under surface of the pack rather than collecting as visible droplets. Antifogging agents include fatty acid esters [87].

## 9.5 Hybrid Polymers in Packaging Applications

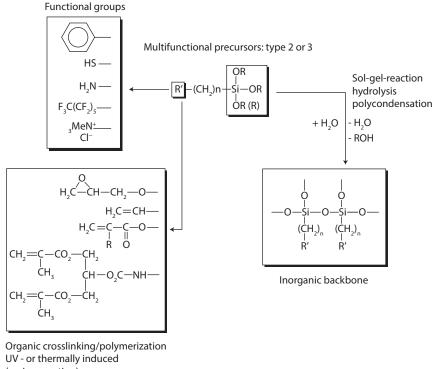
There has been a growing interest and effort over the last few years in the development of novel food packaging concepts, which can play a proactive role regarding product preservation, shelf life extension, and even improvement. Prolonging shelf life involves retardation of enzymatic, microbial, and biochemical reactions through various strategies such as temperature control; moisture control; addition of chemicals such as salt, sugar, carbon dioxide, or natural acids; removal of oxygen; or a combination of these with effective packaging. The ideal packaging material should be inert and resistant to hazards and should not allow molecular transfer from or to packaging materials [88]. Traditional food packages which include metal, ceramic (glass) and paper are passive barriers designed to delay the adverse effects of the environment on the food product [89,90]. While these materials are still used, the light weight, low cost, ease of processing and formability, and remarkable diversity in physical properties of organic polymeric materials make plastics attractive alternatives for the packaging of foods. Though polymers have revolutionized the food industry and possess numerous advantages over conventional materials, their major drawback is an inherent permeability to gasses and other small molecules [75]. Several new strategies have been formulated to exert a positive action over the packaged foodstuff, including retention of desirable molecules (i.e., aldehydes, oxygen) and release of substances (i.e., carbon dioxide, aromas) [91]. Extensive studies have been conducted to develop hybrid inorganic-organic polymers as packaging materials to keep the freshness of food along with extending its shelf life. This includes development of inorganic-organic hybrid polymers either based on sol-gel technique or via polymers filled with inorganic particles, or layered inorganic compounds intercalated by organic polymers. In these classes of inorganic-organic hybrid materials, the constituents are connected with each other by strong covalent or ionic bonds. Other nanotechnology innovations in the forms

of pathogen detection, active packaging, antimicrobial packaging and barrier formation are also poised to elevate food packaging to new heights [4,92].

### 9.5.1 Hybrid Inorganic-Organic Polymers

Due to the possibility of combining characteristics of inorganic moieties and organic polymers, materials exhibiting exceptional properties such as transparency, good adhesion, barrier effect and corrosion protection, adjustable mechanical properties, decorative properties, and functional properties can be created. Class II sol-gel hybrid materials are one of the promising examples of this category. The main interest in these hybrid materials is as barrier coating systems to develop much more sophisticated materials for food packaging [14]. It seems particularly attractive because it presents several advantages such as high purity of the reactants and of the resulting products; mild processing conditions (low temperature, atmospheric pressure); possible control of connectivity and morphology by suitable choice of reactants, catalyst, and reaction conditions; easy application to any kind of substrate; transparency due to the nanosized organic and inorganic domains; and easy inclusion of inorganic salts in the starting solution to obtain a homogeneous dispersion. Moreover, by a suitable choice of the organic-phase precursor it should also be possible to adjust the mechanical properties of the coating, its morphology, and the adhesion of the coating to the plastic substrate. As a consequence, the diffusion rate of the included additives may in principle be controlled in order to prepare coatings able to release the trapped functional additives at the desired rate. Indeed, the possibility of preparing bioactive materials by using materials obtained by the sol-gel approach has also been recently proposed [93–95].

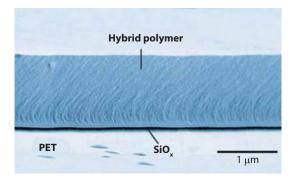
Recent developments in food packaging materials trends range from the fabrication of passive barrier coatings to active coatings that can interact with the packaged items, or even to the development of so-called smart packages that can monitor the conditions of packaged foodstuff [96]. New barrier coating materials based on ORMOSILs have been developed which act as an adhesive/sealing layer barrier against water vapor and gases, as well as an outside layer for weatherability. The building principle of these hybrid polymers is the sol-gel method employing different types of precursor molecules. The first sol-gel process is then followed by organic cross-linking (self, thermal or UV curing systems) or polymerization. Scheme 9.2 illustrates the steps of ORMOSIL synthesis [97,98].



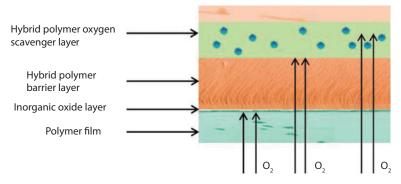
(curing reaction)

Scheme 9.2 ORMOSIL synthesis (reproduced with permission from [97]).

Thus the basis of most of the barrier coatings is polycondensation of some percentage of Al alkoxides with phenyl- and epoxyfunctionalized alkoxysilanes. Due to control of the inorganic and organic network densities and by insertion of specific functional groups, it is possible to vary the material property in a wide range [99]. The barrier efficiency for these hybrid materials is related to the density of the hybrid coating, and can be managed varying the sol-gel chemistry conditions (hydrolysis rate) and oxide content. Furthermore, hybrid material compared to pure inorganic material allows one to enhance the chemical resistance through incorporation of hydrophobic surface functions, such as methyl groups, which also reduce coating stress, allowing a thicker film deposition onto eventually deformable substrates [100–106]. Hybrid polymers formed by sol-gel process are generally amorphous materials. Since there is no crystalline phases present in the structure, these polymers show high optical transparency, which is advantageous for food packaging applications [107]. Comparing the stiffness of typical carbon-based polymers (~5GPa) with



**Figure 9.5** Hybrid coatings as barrier systems. Scanning transmission micrograph of a thin hybrid polymer coating on SiOx deposited on a flexible PET film (reproduced with permission from [112]).



**Figure 9.6** Passive-active barrier coating concept (reproduced with permission from [113]).

inorganic silicon oxides (~70GPa), a combination of organic and inorganic systems gives materials with relatively high stiffness [108–110]. Al-O-Albased epoxy silanes are reported to have high mechanical abrasion resistance [111]. While inorganic oxides have extremely low permeation rates for gases and water vapor, organic polymers have more flexible, open type networks, and hence suffer from high gas permeation when used for packaging application. The permeation of oxygen and water vapor drastically reduces when SiO<sub>x</sub>- and AlO<sub>x</sub>-based hybrid polymer coating [112] is used as a barrier system, as illustrated by Figure 9.5. Concerning oxygen permeability, improvement factors from 30 to 300 were obtained depending on the coating support.

A revolutionary concept called passive-active barrier coating (refer to Figure 9.6) prepared by sol-gel method was developed by major chemical

companies. A new combined oxygen scavenger system formed in a onestep synthesis by hydrolysis of the corresponding alkoxysilanes is used for integration into packaging film materials to remove oxygen by means of the oxygen scavenger component. The functional principle of the newly developed oxygen scavenger system is based on a photoinitiated, metalcatalyzed oxidation of a cyclo-olefin bonded chemically to a silicate backbone. This concept permits the activation of the scavenging process by UV light and prevents the formation of low-molecular-weight oxidation products which may decrease the quality of the packaged goods or may even be toxic. Such active layers can be deposited on any inorganic or organic surface [113].

In addition to their barrier properties against gases, inorganic-organic polymers can be used as protective layers against migration of chemical substances and for other additional functionalities [106].

The chemistry of ORMOSILs can also be tailored to have antimicrobial property in the coating formulations. When antimicrobial agents like ammonium silanes are fixed to the hybrid network by covalent bonding, microbes which have direct contact with the surface cannot grow and are subsequently effectively inhibited. The release mechanism works by incorporating active agents like benzoic acid in such a way as to allow its diffusion into the surroundings, thus retarding microbe attack [112].

Silver-doped organic-inorganic hybrid coatings were developed starting from tetraethoxysilane- and triethoxysilane-terminated poly(ethylene glycol)-*block*-polyethylene by the sol-gel process for food packaging polymer materials. In addition to the good antibacterial properties observed, the coated films showed the same transparency as the uncoated ones (due to the nanosized organic and inorganic domains) and quite good adhesion to both polyethylene and poly(vinyl chloride) substrates, even without any preliminary treatment of the plastic film surfaces [114].

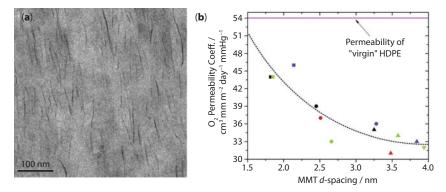
The recent developments for smart packaging include oxygen indicators, freshness indicators and pathogen sensors based on functional materials incorporated in the active barrier coating.

#### 9.5.2 Polymer Nanocomposites

Recent studies have shown that at smaller dimensions, materials can be controlled at a greater extent, and hence research on application of nanomaterials (scale of 1–100 nm) in packaging is exponentially increasing [115]. In general, the unique combination of the nanomaterial's characteristics such as size, mechanical properties, and low concentrations necessary to effect change in a polymer matrix, coupled with the advanced characterization and simulation techniques now available, have generated much interest in the field of polymer nanocomposites. In addition, many polymer nanocomposites can be fabricated and processed in ways similar to that of conventional polymer composites, making them particularly attractive from a manufacturing point of view [116].

Polymer nanocomposites are created by dispersing an inert, nanoscale filler throughout a polymeric matrix. Filler materials can include clay and silicate nanoplatelets silica (SiO<sub>2</sub>) nanoparticles [117–120], carbon nanotubes [121-126], graphene [127,128] and other inorganics. Melt processing, in-situ polymerization and solution-based processing techniques are employed for the preparation of different filler/polymer nanocomposite systems [129-131]. Polymer nanocomposites-based packaging materials have several valuable properties as packaging materials for improving food quality and extending the shelf life through minimizing microbial growth in the product [115]. Nanocomposites exhibit increased barrier properties, increased mechanical strength, and improved heat resistance compared to their neat polymers and conventional composites [130,131]. Also, because of their improved mechanical properties, nanocomposites may allow down-gauging, thus reducing materials usage. Nanocomposites may even offer environmental advantages over conventional plastics. For instance, when a nanofiller is dispersed within the biocompatible polymer polylactic acid (PLA), the nanocomposite actually has a faster rate of biodegradation than PLA containing no such additives [132]. In addition to serving as barriers to water vapor, gases, and solutes, they can also act as carriers of some active substances such as oxygen scavengers, antimicrobial agents, moisture absorbers and nanosensors for food quality measurement [56]. In summary, the main applications for polymer nanocomposites for food packaging will be "improved" (where the nanoparticles in the polymer matrix improve the properties of packaging flexibility, barrier property and thermal resistance); "active" (the presence of nanoparticle allows packages to interact with the food environment); and "intelligent/smart" (nanoparticles as nanosensors to monitor the conditions of packaged food) [76].

Polymers incorporating clay nanoparticles are among the first polymer nanomaterials to emerge on the market as improved materials for food packaging. Clay nanoparticles have a nanolayer structure with the layers separated by interlayer spaces [133–135]. Their dimensions, 1 nm thick and 100 to 500 nm in diameter, result in platelets of high aspect ratio [136]. The effect of nanoclay minerals on polymer properties originate mainly from their high surface area to volume ratio, since polymer-filler interactions are governed by interfacial forces. Clay particles should be exfoliated



**Figure 9.7** (a) TEM image of PA6/5% C30B nanocomposites showing exfoliated clay platelets; (b) Effect of clay organic modifier on the barrier properties of high density poly(ethylene) (HDPE) matrix. MMT clays were chemically modified with trimethyl-(octadecyl)ammonium [ð], dimethyldi(octadecyl)ammonium [o], methyl-tri (octadecyl) ammonium [ $\Delta$ ] and tetra(octadecyl)ammonium [ $\nabla$ ] surfactants (reproduced with permission from [75,133]).

as individual platelets and uniformly dispersed within the polymer matrix in order to take full advantage of the potential high surface area [134]. The clay minerals are generally organically modified with surfactants to increase the compatibility with hydrophobic polymer matrices and exfoliation. Exfoliated nanoclay layers are effective at improving gas and water vapor barrier properties of polymeric materials [75,137]. When dispersed into polymers, they create a maze structure that presents a tortuous path to moving gases, greatly slowing their permeation rate (refer to Figure 9.7) [138]. It is well known that clay particles are effective nucleating agents which greatly change the crystalline morphology and crystal type for polymers like nylon 6 or polypropylene, which can also affect the barrier properties of pristine polymers [139].

Properly dispersed and aligned clay platelets have proven to be very effective for increasing mechanical properties such as strength and modulus of the nanocomposites. Traditional composite structures contain large quantities of filler (approximately 60% vol), whereas in polymer nanocomposites, dramatic changes in properties are possible at very low loadings (< 10 vol%) [140]. The significant improvements of tensile strength and tensile modulus given by the exfoliated clay minerals on polymer nanocomposites were first reported by Toyota researchers [141]. The tensile strength of polyamide-6 was increased by 55% and the modulus by 90% with the addition of only 4 wt% of delaminated clay. More than a 10-fold increase in strength and modulus in a rubbery epoxy matrix with only 15

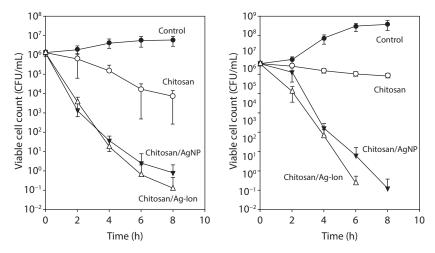
wt% of delaminated organically modified clay minerals [142] was reported later on. A 30% increase of tensile modulus could be obtained in partially delaminated unsaturated polyester-clay nanocomposite with 5 vol% of clay mineral content [75].

Other benefits have been reported on the performance of a diversity of polymers resulting from using clay nanoparticles, including increased glass transition [143–145] and thermal degradation temperatures [145–147], with a minor disadvantage of decreased transparency [145]. Toyota was the first company to commercialize nanocomposite materials, and they found that the addition of 5 wt% nanosized montmorillonite clay significantly increased the thermal properties of different grades of nylon [148]. This property was combined with a reduction in the thermal expansion coefficient up to 45%. The improvement of heat distortion temperature increased with the length and the content of silicate layers, and was attributed to the presence of a constrained region in the nanocomposites [56].

There are several reports on polymer nanocomposites containing carbon nanotubes and graphene nanoplates with improved heat resistant, high barrier nanocomposites with improved mechanical properties that are promising in food packaging applications. However, the use of these fillers in nanocomposites, to date, has been limited by challenges in processing and dispersion, and their exorbitantly high cost [140,149].

Active packaging is designed to integrate constituents (nanoparticles) that would interact with the packaged food or with the environment surrounding the food. At present, active packaging has been mainly advanced for antimicrobial packaging applications [140]. One of the biggest advantages of inorganic nanoparticles over molecular antimicrobials is the ease with which the former can be incorporated into polymers to form functional antimicrobials. These nanocomposites can be engineered to remain potent antimicrobial agents for long periods of time, which in turn can increase the shelf life of packed foodstuff [150,151]. Other main promising applications of active packaging include oxygen scavengers, ethylene removers and carbon dioxide absorbers/emitters [152].

Silver is the most studied metal nanoparticle with antimicrobial function since it has temperature stability, low volatility and significantly high antimicrobial activity against a wide range of fungi and bacteria [153,154]. Silver nanocomposites have been obtained by several researchers and their antimicrobial effectiveness has been extensively reported (refer to Figure 9.8) [155–160]. Synergic effect of bimetallic systems containing silver and gold in conjunction with zeolite minerals was also found to produce a greater antibacterial effect than silver alone [161]. Nanoparticles of zinc [162], copper [163], as well as carbon nanotubes [164,165] have also been



**Figure 9.8** Antimicrobial of silver/chitosan nanocomposites against different pathogenic bacteria: (a) *S. Aureus* and (b) *E. coli* (reproduced with permission from [158]).

reported as antimicrobial, antibiotic and antifungal agents when incorporated into plastic matrix. Among other nanoparticles with antimicrobial property,  $\text{TiO}_2$  nanoparticles have been widely investigated. Unlike silver nanoparticles,  $\text{TiO}_2$  nanoparticles are only active in the presence of UV light. In principle, food packaging films incorporating  $\text{TiO}_2$  nanoparticles may have the additional benefit of protecting food content from the oxidizing effects of UV irradiation while maintaining good optical clarity, as  $\text{TiO}_2$  nanoparticles are efficient short-wavelength light absorbers with high photostability [166–170]. Lately, antimicrobial properties of nanostructured metal oxides such as ZnO, CuO and MgO have been revealed [171–176]. Compared to nanosilver, the nanoparticles of ZnO and MgO are expected to provide more affordable and safe food packaging solutions in the future. The ZnO nanoparticles do not require UV light to be active; rather they are stimulated by visible light [177].

The presence of  $O_2$  in a package can trigger or accelerate oxidative reactions that result in food deterioration and facilitate the growth of aerobic microbes and molds. Oxidation reactions in turn result in undesirable odors, flavors, color changes, and reduced nutritional quality of packaged food. Oxygen-scavenging compounds are mostly agents that react with oxygen to reduce its concentration. Ferrous oxide is the most commonly used scavenger [178]. Several nanoparticles, including TiO<sub>2</sub> nanoparticles, were used to produce oxygen-scavenger films. Others include ascorbic acid, sulfites, catechol, some nylons, photosensitive dyes, unsaturated hydrocarbons, ligands, and enzymes such as glucose oxidase [90]. The most studied

oxide nanoparticle additives for packaging polymers are  $TiO_2$ , ZnO,  $SiO_2$  and MgO, due to their ability to be UV blockers and photocatalytic disinfecting agents [179]. Some nanoparticles based on silver that have antimicrobial activity are also able to absorb and decompose ethylene, thereby helping to extend the shelf life of fruits and vegetables [180].

Intelligent or smart packaging is designed to monitor the environment of the food and communicate information about its quality [89,178]. Examples include time-temperature indicators (TTIs), ripeness indicators, biosensors, and radio frequency identification (RFID). Nanoparticles can be applied as reactive particles in packaging materials to inform about the state of the package, thereby helping consumers to determine whether the food is palatable. The so-called nanosensors are able to respond to environmental changes (e.g., temperature or humidity in storage rooms, levels of oxygen exposure), degradation products or microbial contamination [181].

The unique chemical and electro-optical and gas sensing properties of nanoscale particles is the basis of such technological development. When incorporated into food packaging, nanosensors can identify certain chemical compounds, pathogens, and toxins in food, thus being useful in providing the real-time status of food freshness and eliminating the need for information on expiration dates. The recent developments in nanoparticle-based food packaging sensors include oxygen indicators, freshness indicators and pathogen sensors [182]. For example, functionalized gold nanoparticles selectively bind to melamine and this causes aggregation of gold nanoparticles which leads to a color change from red to blue. This can be used to precisely measure the melamine content in raw milk and infant formula at concentrations as low as 2.5 ppb [183]. Photoactivated indicator ink based on TiO<sub>2</sub>, SnO<sub>2</sub> nanoparticles and a redox active dye (e.g., methylene blue) has been developed as an oxygen indicator for packaging films [184,185]. Other gas sensors include a series of electronic ZnO-TiO, nanocomposites, SnO nanobelts, to detect the presence of volatile organics, including acetone, ethanol and carbon monoxide [186,187]; and WO,-SnO<sub>2</sub> nanocomposites to detect the presence of ethylene gas, a hormone responsible for fruit ripening [188]. Sensor systems based on nanomaterials such as cerium oxide [189], carbon nanotubes [190,191] have been investigated for the detection of various biomolecules formed in the packaging environment.

A considerable amount of research is also focusing on biodegradable nanocomposite food packages. Exploration of edible film packaging and biobased packaging materials from renewable sources are also highly encouraged these days. This new class of materials is reported to have enhanced barrier, mechanical and thermal properties and has been considered as a promising alternative to synthetic plastic packaging materials [131,192–196]. Renewable resource-based biopolymers such as starch, cellulosic plastics, corn-derived plastics such as polylactide (PLA), and polyhy-droxyalkanoates (PHAs) are some of the most widely used biopolymers to produce nanocomposites for food packaging applications. The most promising nanoscale fillers used in bionanocomposite preparation are layered silicate nanoclays such as montmorillonite and kaolinite. Moreover, similar to the nanostructures used in petroleum-based polymer matrices, several nanostructures are used to provide active and/or smart properties to biobased food packaging systems, as exemplified by antimicrobial properties, oxygen scavenging ability, etc. [160].

## 9.6 Current Status and Future Prospects

Hybrid inorganic-organic materials form a remarkable and growing category within the realm of materials for food packing application [5]. The increasing demand for new food packaging materials which fulfill consumer demands has provided the thrust for improving the inherent properties of these materials. A combination of various organic polymers and inorganic materials has been very useful for the exploration of new materials having unique properties and specific performances when compared to individual constituents. Although conventional, macroscopic hybrid materials have ruled the world for many decades, the realization that reduction in domain size of inorganic phase to 100 nm or below will result in dramatic changes in the structure and hence properties of the material has led to the development of a new field called "polymer nanotechnology." With the advancement of this technology, processing and characterization tools, it is now possible to have a high degree of control of both composition and structure of these materials, which in turn results in high performance and multifunctional polymeric materials. Applications of polymer nanotechnology can, in fact, provide new food packaging materials (based on sol-gel-based hybrids, polymer nanocomposites and bionanocomposites) with improved mechanical, barrier and antimicrobial properties, together with nanosensors for tracing and monitoring the condition of food during transport and storage [152]. Hybrid materials obtained by mixing polymers and sheets of crystalline solid layered (clays or LDHs) or nanoparticle materials (Ag, TiO, and ZnO) are of particular interest nowadays because of their great improvement in mechanical, thermal, barrier as well as antimicrobial properties over conventional composites.

The progress in food packaging materials has mostly been concentrated on ultra-high barrier properties, oxygen scavenging and controlling moisture migration, microbial growth, respiration rates, and volatile flavors and aromas. This focus parallels the development in sustainable packaging, using bionanocomposites derived from renewable sources. The innovations in the form of nanoparticles for pathogen detection, active packaging, and barrier formation have taken food packaging to higher levels.

However, the use of nanomaterial-based food packaging has raised numerous safety, ecological and regulatory concerns. The main question is regarding the possible migration of nanoparticles from packaging material to foodstuff and their ultimate toxicological effect on human health. Although nanomaterials offer exciting benefits in terms of food packaging property enhancement, the potential risks associated with these materials have either not been evaluated or are still being evaluated. Acceptable test methods should be developed for the risk analyses of nano-based packaging materials which are intended to be used under specific storage conditions. The packaging industry is also expected to not only assure product quality adhering to regulatory rules, but also to offer accurate information about the benefits and risks of the materials to end users.

A wide variety of inorganic-organic hybrid polymers and nanocomposites are available as food packaging materials, and the number of material choices will continue to grow in the future. A holistic approach integrating materials, processes, usage, disposal and balancing cost, performance, health and environmental considerations is envisaged for the future development of these materials. Although a significant amount of research is being undertaken in packaging materials worldwide, further developments in the basic understanding and manipulation of hybrid polymers with fascinating multifunctional properties seem to be promising to achieve highly advanced systems for the food industry. Once the aforementioned barriers are crossed, there is no doubt that the global market and consumers can enjoy the benefits of these sophisticated food packaging materials.

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# References

- 1. Sanchez, C., Belleville, P., Popall, M., Nicole, L. Applications of advanced hybrid organic-inorganic nanomaterials: From laboratory to market. *Chem Soc Rev* 40:696–753, 2011.
- 2. Haas, K., Amberg-Schwab, S., Rose, K. Functionalized coating materials based on inorganic-organic polymers. *Thin Solid Film* 351:198–203, 1999.
- 3. Kickelbick, G. Concepts for the incorporation of inorganic building blocks into organic polymers on a nanoscale. *Prog Polym Sci* 28:83–114, 2003.
- 4. Schubert, U. Polymers reinforced by covalently bonded inorganic clusters. *Chem Mater* 3:3487–94, 2001.
- 5. Sanchez, C., Rozes, L., Ribot, F., Laberty-Robert, C., Grosso, D., Sassoye, C., *et al.* 'Chimie douce:' A land of opportunities for the designed construction of functional inorganic and hybrid organic-inorganic nanomaterials. *C R Chimie* 13:3–39, 2010.
- Sanchez, C., Soler-Illia, G. J.d. A., Ribot, F., Lalot, T., Mayer, C. R., Cabuil, V. Designed hybrid organic-inorganic nanocomposites from functional nanobuilding blocks. *Chem Mater* 13:3061–83, 2001.
- Arkles, B. Commercial applications of sol-gel-derived hybrid materials. MRS Bull 26:402–8, 2001.
- Livage, J., Lemerle, J. Transition-metal oxide gels and colloids. Annu Rev Mater Sci 12:103–22, 1982.
- 9. Kickelbick, G. Introduction to hybrid materials. In *Hybrid Materials: Strategies, Syntheses, Characterization and Applications*, ed. G. Kickelbick, pp. 1–47. Weinheim: Wiley-VCH, 2007.
- 10. Chujo, Y. Organic-inorganic nano-hybrid materials. Kona 25:255, 2007.
- 11. Livage, J., Sanchez, C. Sol-gel chemistry. J Non-Cryst Solids 145:11–9, 1992.
- Gómez-Romero, P., Sanchez, C. Hybrid materials, functional applications: An Introduction. In *Functional Hybrid Materials*, eds. P. Gómez-Romero and C. Sanchez, pp. 1–10. Weinheim: Wiley-VCH, 2004.
- 13. Hench, L. L., West, J. K. The sol-gel process. Chem Rev 90 (1): 33-72, 1990.
- Sanchez, C., Julián, B., Belleville, P., Popall, M. Applications of hybrid organicinorganic nanocomposites. J Mater Chem 15 (35–36): 3559–92, 2005.
- 15. Judeinstein, P., Sanchez, C., Hybrid organic–inorganic materials: A land of multidisciplinarity. *J Mater Chem* 6 (4): 511–25, 1996.
- 16. Schubert, U., Hüsing, N. *Synthesis of Inorganic Materials*, pp. 1-429. Weinheim: Wiley-VCH, 2000.
- 17. Sadjadi, M., Farhadyar, N., Zare, K. Preparation and characterization of the transparent nanocomposite mirror film for the infrared region by sol-gel method. *Superlattice Microst* 46:483–9, 2009.
- 18. Gomez-Romero, P. Hybrid organic-inorganic materials in search of synergic activity. *Adv Mater* 13:5, 2001.
- 19. Sinha Ray, S., Okamoto, M. Polymer/layered silicate nanocomposites: A review from preparation to processing. *Progr Polym Sci* 28:1539–641, 2003.

- Gain, O., Espuche, E., Pollet, E., Alexandre, M., Dubois, P. Gas barrier properties of poly (ε-caprolactone)/clay nanocomposites: Influence of the morphology and polymer/clay interactions. *J Polym Sci Part B: Poly Phys* 43:205–14, 2005.
- Gorrasi, G., Tortora, M., Vittoria, V., Pollet, E., Alexandre, M., Dubois, P. Physical properties of poly (ε-caprolactone) layered silicate nanocomposites prepared by controlled grafting polymerization. *J Polym Sci Part B: Polym Phys* 42:1466–75, 2004.
- Picard, E., Vermogen, A., Gérard, J., Espuche, E. Barrier properties of nylon 6-montmorillonite nanocomposite membranes prepared by melt blending: Influence of the clay content and dispersion state: Consequences on modelling. *J Membr Sci* 292:133–44, 2007.
- 23. Alexandre, M., Dubois, P. Polymer-layered silicate nanocomposites: Preparation, properties and uses of a new class of materials. *Mater Sci Eng:* R 28:1–63, 2000.
- 24. Azeredo, H. Nanocomposites for food packaging applications. *Food Res Int* 42:1240–53, 2009.
- Nagata, K., Kodama, S., Kawasaki, H., Deki, S., Mizuhata, M. Influence of polarity of polymer on inorganic particle dispersion in dielectric particle/ polymer composite systems. *J Appl Polym Sci* 56:1313–21, 1995.
- 26. Schmidt, H., Wolter, H. Organically modified ceramics and their applications. J Non-Cryst Solids 121:428–35, 1990.
- 27. Zhang, Q., Que, W., Buddhudu, S., Pita, K. An efficient lasing action from pyrromethene 556 dye-doped organically modified silicates. *J Phys Chem Solids* 63:1723–7, 2002.
- 28. Huang, H., Orler, B., Wilkes, G. L. Ceramers: Hybrid materials incorporating polymeric/oligomeric species with inorganic glasses by a sol-gel process. *Polym Bull* 14:557–64, 1985.
- 29. Wilkes, G., Orler, B., Huang, H. Ceramers: Hybrid materials incorporating polymeric/oligomeric species with inorganic glasses by a sol-gel process. *Polym Bull* 14:557, 1985.
- Camargo, P. H. C., Satyanarayana, K. G., Wypych, F. Nanocomposites: Synthesis, structure, properties and new application opportunities. *Mater Res* 12:1–39, 2009.
- 31. In, M., Gérardin, C., Lambard, J., Sanchez, C. Transition metal based hybrid organic-inorganic copolymers. *J Sol-gel Sci Tech* 5:101–14, 1995.
- 32. Soler-Illia. G. J.d. A., Sanchez, C., Lebeau, B., Patarin, J. Chemical strategies to design textured materials: From microporous and mesoporous oxides to nanonetworks and hierarchical structures. *Chem Rev* 102:4093–138, 2002.
- 33. Drisko, G. L., Sanchez, C. Hybridization in materials science–evolution, current state, and future aspirations. *Eur J Inorg Chem* 2012:5097–105, 2012.
- 34. Steunou, N., Robert, F., Boubekeur, K., Ribot, F., Sanchez, C. Synthesis through an in situ esterification process and characterization of oxo isopropoxo titanium clusters. *Inorg Chim Acta* 279:144–51, 1998.

- Bourget, L., Corriu, R., Leclercq, D., Mutin, P., Vioux, A. Non-hydrolytic solgel routes to silica. J Non-Cryst Solids 242:81–91, 1998.
- 36. Judeinstein, P. Hybrid materials: Intricate structures guiding complex dynamics. *MRS Proceed* 519:151, 1994.
- Schubert, U., Huesing, N., Lorenz, A. Hybrid inorganic-organic materials by sol-gel processing of organofunctional metal alkoxides. *Chem Mater* 7:2010– 27, 1995.
- 38. Loy, D. A., Shea, K. J. Bridged polysilsesquioxanes: Highly porous hybrid organic-inorganic materials. *Chem Rev* 95:1431–42, 1995.
- Landry, C. J., Coltrain, B. K., Brady, B. K. In situ polymerization of tetraethoxysilane in poly (methyl methacrylate): Morphology and dynamic mechanical properties. *Polymer* 33:1486–95, 1992.
- Ribot, F., Sanchez, C. Organically functionalized metallic oxo-clusters: Structurally well-defined nanobuilding blocks for the design of hybrid organic-inorganic materials. *Comments Inorg Chem* 20:327–71, 1999.
- Pope, E., Asami, M., Mackenzie, J. Transparent silica gel-PMMA composites. *J Mater Res* 4:1018–26, 1989.
- 42. Schubert, U. New materials by sol-gel processing: Design at the molecular level. *J Chem Soc: Dalton Trans* 16:3343–8, 1996.
- Zhang, M. Q., Rong, M. Z., Friedrich, K. Processing and properties of nonlayered nanoparticles reinforced thermoplastic composites. In *Handbook of Organic–Inorganic Hybrid Materials and Nanocomposites*, ed. H. S. Nalwa, pp. 113–150. USA: American Scientific Publishers, 2003.
- Wang, S., Yang, S., Yang, C., Li, Z., Wang, J., Ge, W. Poly (N-vinylcarbazole) (PVK) photoconductivity enhancement induced by doping with CdS nanocrystals through chemical hybridization. *The J Phys Chem B* 104:11853–8, 2000.
- Sheng, W., Kim, S., Lee, J., Kim, S., Jensen, K., Bawendi, M. G. In-situ encapsulation of quantum dots into polymer microspheres. *Langmuir* 22:3782–90, 2006.
- Park, J. H., Park, O. O., Kim, S. Photoelectrochemical water splitting at titanium dioxide nanotubes coated with tungsten trioxide. *Appl Phys Lett* 89:163106, 2006.
- Pan, F., Cheng, Q., Jia, H., Jiang, Z. Facile approach to polymer-inorganic nanocomposite membrane through a biomineralization-inspired process. J Membr Sci 357:171–7, 2010.
- Pomogailo, A. D., Kestelman, V. N. Chemical methods of metal-polymer nanocomposite production. In *Metallopolymer Nanocomposites*. Springer series in materials science, eds. A. D. Pomogailo, and V. N. Kestelman, pp. 135–236. Berlin: Springer, 2005.
- 49. Balan, L., Burget, D. Synthesis of metal/polymer nanocomposite by UV-radiation curing. *Eur Polym J* 42:3180–9, 2006.

- Kango, S., Kalia, S., Celli, A., Njuguna, J., Habibi, Y., Kumar, R. Surface modification of inorganic nanoparticles for development of organic–inorganic nanocomposites: A review. *Prog Polym Sci* 38:1232–61, 2013.
- 51. Brinker, C., Hurd, A., Schunk, P., Frye, G., Ashley, C. Review of sol-gel thin film formation. *J Non-Cryst Solids* 147:424–36, 1992.
- 52. Jordan, J., Jacob, K. I., Tannenbaum, R., Sharaf, M. A., Jasiuk, I. Experimental trends in polymer nanocomposites: A review. *Mater Sci Eng: A* 393:1–11, 2005.
- Hernandez, R. J., Selke, S. E., Culter, J. D., Culter, J. Plastics Packaging: Properties, Processing, Applications, and Regulations, pp. 1–3. Carl Hanser Verlag: Munich, 2004.
- López-Rubio, A., Lagarón, J. M., Hernández-Muñoz, P., Almenar, E., Catalá, R., Gavara, R. Effect of high pressure treatments on the properties of EVOHbased food packaging materials. *Innov Food Sci Emerg Technol* 6:51–8, 2005.
- 55. Ahvenainen, R., Hurme, E. Active and smart packaging for meeting consumer demands for quality and safety. *Food Addit Contam* 14:753–63, 1997.
- 56. Youssef, A M. Polymer nanocomposites as a new trend for packaging applications. *Polym-Plast Technol Eng* 52:635–60, 2013.
- Mrkić, S., Galić, K., Ivanković, M., Hamin, S., Ciković, N. Gas transport and thermal characterization of mono-and di-polyethylene films used for food packaging. *J Appl Polym Sci* 99:1590–9, 2006.
- Galic, K., Cikovic. N. The effect of liquid absorption on gas barrier properties of triplex film coated with silicon oxide. *Food Technol Biotechnol* 41(3):247– 52, 2003.
- Galotto, M., Ulloa, P., Hernández, D., Fernández-Martín, F., Gavara, R., Guarda, A. Mechanical and thermal behaviour of flexible food packaging polymeric films materials under high pressure/temperature treatments. *Packag Technol Sci* 21:297–308, 2008.
- 60. Chatham, H. Oxygen diffusion barrier properties of transparent oxide coatings on polymeric substrates. *Surf Coat Technol* 78:1–9, 1996.
- 61. Siracusa, V. Food packaging permeability behaviour: A report. *Int J Polym Sci 2012*: Article ID 302029, 2012.
- Gajdoš, J., Galić, K., Kurtanjek, Ž., Ciković, N. Gas permeability and DSC characteristics of polymers used in food packaging. *Polym Test* 20:49–57, 2000.
- Beaudry, R. M., Cameron, A. C., Shirazi, A., Dostal-Lange, D. L. Modifiedatmosphere packaging of blueberry fruit: Effect of temperature on package O<sub>2</sub> and CO<sub>2</sub>. J Am Soc Hortic Sci 117:436–41, 1992.
- 64. Wijmans, J., Baker, R. The solution-diffusion model: A review. *J Membr Sci* 107:1–21, 1995.
- Favre, E., Nguyen, Q., Schaetzel, P., Clement, R., Neel, J. Sorption of organicsolvents into dense silicone membranes. *J Chem Soc Faraday Trans* 89:4439, 1993.

- 66. Stannett, V. The transport of gases in synthetic polymeric membranes: An historic perspective. *J Membr Sci* 3:97–115, 1978.
- 67. Crank, J. Methods of measurement. In *Diffusion in Polymers*, eds. JJ. Crank, G. S. Park, pp. 1–39. Academic Press: New York, 1968.
- 68. ASTM D 1434: Standard testing method for determining gas permeability characteristics of plastic film and sheeting, west conshohocken. ASTM International, 2003.
- 69. Pauly, S. Premeability and diffusion data. In *Polymer Handbook*, eds. J. Brandrup, E. H. Immergut, E. A. Grulke, p. 56. New York, USA: John Wiley & Sons, 1989.
- Brown, H., Williams, J. Packaged product quality and shelf life. In Food Packaging Science and Technology, eds. D. S. Lee, K. L. Yam, and L. Piergiovanni, p. 69. CRC Press, Taylor & Francis Group, 2008.
- Gagnard, C., Germain. Y., Keraudren. P., Barrière, B. Permeability of semicrystalline polymers to toluene/methanol mixture. *J Appl Polym Sci* 92:676– 82, 2004.
- Russo, G., Simon, G., Incarnato, L. Correlation between rheological, mechanical, and barrier properties in new copolyamide-based nanocomposite films. *Macromol* 39:3855–64, 2006.
- 73. Siracusa, V., Rocculi, P., Romani, S., Rosa, M. D. Biodegradable polymers for food packaging: A review. *Trends Food Sci Technol* 19:634–43, 2008.
- 74. Pavlidou, S., Papaspyrides, C. A review on polymer-layered silicate nanocomposites. *Prog Polym Sci* 33:1119–98, 2008.
- Duncan, T. V. Applications of nanotechnology in food packaging and food safety: Barrier materials, antimicrobials and sensors. *J Colloid Interface Sci* 363:1–24, 2011.
- 76. Zeman, S. Mechanical properties to measure resistance of food packaging materials to external influences. *Tech Sci* 10:35, 2007.
- Auras, R. A., Singh, S. P., Singh, J. J. Evaluation of oriented poly (lactide) polymers vs. existing PET and oriented PS for fresh food service containers. *Packag Technol Sci* 18:207–16, 2005.
- 78. Han, JH. Antimicrobial food packaging. Food Technol 54:50-70, 2003.
- 79. Matthews, F. L., Rawlings, R. D. Ceramic matrix composites. In *Composite Materials: Engineering and Science*, p. 137. London: Chapman and Hall, 1994.
- Majeed, K., Jawaid, M., Hassan, A., Abu Bakar, A., Abdul Khalil, H., Salema, A., *et al.* Potential materials for food packaging from nanoclay/natural fibres filled hybrid composites. *Mater Des* 46:391–410, 2013.
- Azizi Samir, M. A. S., Alloin, F., Dufresne, A. Review of recent research into cellulosic whiskers, their properties and their application in nanocomposite field. *Biomacromol* 6:612–26, 2005.
- Dalmas, F., Cavaillé, J., Gauthier, C., Chazeau, L., Dendievel, R. Viscoelastic behavior and electrical properties of flexible nanofiber filled polymer nanocomposites: Influence of processing conditions. *Compos Sci Technol* 67:829– 39, 2007.

- Dubief, D., Samain, E., Dufresne, A. Polysaccharide microcrystals reinforced amorphous poly (β-hydroxyoctanoate) nanocomposite materials. *Macromol* 32:5765–71, 1999.
- Hussain, F., Hojjati, M., Okamoto, M., Gorga, RE. Review article: Polymermatrix nanocomposites, processing, manufacturing, and application: An overview. J Compos Mater 40:1511–75, 2006.
- 85. ASTM D882-02: Standard test method for tensile properties of thin plastic sheeting. ASTM International, West Conshohocken. 2002.
- 86. ASTM D1709-03: *Standard test method for impact resistance of plastic film by the the free-falling dart method.* ASTM International, West Conshohocken. 2004.
- Sablani, S. S., Syamaladevi, R. M., Swanson, B. G. A review of methods, data and applications of state diagrams of food systems. *Food Eng Rev* 2:168–203, 2010.
- 88. Robertson, G. L. Introduction to food packaging. In *Food Packaging Principles and Practices*, ed. GG. Robertson, p. 545. New York, USA: Taylor & Francis, 2006.
- 89. Brody, A. L. Nano and food packaging technologies converge. *Food Technol* 60:92, 2006.
- López-Rubio, A., Hernández-Muñoz, P., Gimenez, E., Yamamoto, T., Gavara, R., Lagarón, J. M. Gas barrier changes and morphological alterations induced by retorting in ethylene vinyl alcohol-based food packaging structures. J Appl Polym Sci 96:2192–202, 2005.
- 91. Lopez-Rubio, A., Gavara, R., Lagaron. J. M. Bioactive packaging: Turning foods into healthier foods through biomaterials. *Trends Food Sci Technol* 17:567–75, 2006.
- Emamifar, A. Application of antimicrobial polymer nanocomposites in food packaging. In *Advances in Nanocomposite Technology*, ed. A. Hashim, p. 299. Croatia: InTech, 2011.
- 93. Dobmeier, K. P., Schoenfisch, M. H. Antibacterial properties of nitric oxidereleasing sol-gel microarrays. *Biomacromol* 5:2493–5, 2004.
- Nablo, B. J., Chen, T., Schoenfisch, M. H. Sol-gel derived nitric-oxide releasing materials that reduce bacterial adhesion. *J Am Chem Soc* 123:9712–3, 2001.
- Marxer, S. M., Rothrock, A. R., Nablo, B. J., Robbins, M. E., Schoenfisch, M. H. Preparation of nitric oxide (NO)-releasing sol-gels for biomaterial applications. *Chem Mater* 15:4193–9, 2003.
- 96. Silvestre, C., Cimmino, S. Polymer nanomaterials for food packaging: Current issues and future trends. In *Eco-sustainable Polymer Materials for Food Packaging*, eds. C. Silvestre, and S. Cimmino, p. 20. New York, USA: Taylor and Francis, 2013.
- Haas, K., Wolter, H. Synthesis, properties and applications of inorganicorganic copolymers (ORMOCERs<sup>®</sup>). *Curr Opin Solid State Mater Sci* 4:571– 80, 1999.

- Brinker, C., Sehgal, R., Hietala, S., Deshpande, R., Smith, D., Loy, D., et al. Sol-gel strategies for controlled porosity inorganic materials. J Membr Sci 94:85–102, 1994.
- Amberg-Schwab, S., Hoffmann, M., Bader, H., Gessler, M. Inorganic-organic polymers with barrier properties for water vapor, oxygen and flavors. *J Solgel Sci Technol* 13:141–6, 1998.
- 100. Kron, J., Amberg-Schwab, S., Schottner, G. Functional coatings on glass using ORMOCER\*-systems. *J Sol-gel Sci Technol* 2:189–92, 1994.
- 101. Haas, K. H. Hybrid inorganic-organic polymers based on organically modified si-alkoxides. *Adv Eng Mater* 2:571–82, 2000.
- 102. Haas, K., Amberg-Schwab, S., Rose, K., Schottner, G. Functionalized coatings based on inorganic-organic polymers (ORMOCER<sup>®</sup> s) and their combination with vapor deposited inorganic thin films. *Surf Coat Technol* 111:72–9, 1999.
- 103. Amberg-Schwab, S., Weber, U., Burger A, Nique, S., Xalter, R. Development of passive and active barrier coatings on the basis of inorganic–organic polymers. *Monatshefte für Chem* 137:657–66, 2006.
- 104. Amberg-Schwab, S., Katschorek, H., Weber, U., Burger, A., Hänsel, R., Steinbrecher, B., *et al.* Inorganic-organic polymers as migration barriers against liquid and volatile compounds. *J Sol-gel Sci Technol* 26:699–703, 2003.
- Amberg-Schwab, S., Arpac, E., Glaubitt, W., Greiwe, K. Process and coating compound for producing UV or UV/IR or IR/UV hardened coatings. US Patent, US5580614 A, 1996.
- 106. Amberg-Schwab, S., Arpac, E., Glaubitt, W., Rose, K., Schottner, G., Schubert, U. Protective coatings for organic polymers by sol-gel techniques. *High Perform Ceram Film Coat* 203–10, 1990.
- 107. Houbertz, R., Schulz, J., Frohlich, L., Domann, G., Popall, M. Inorganicorganic hybrid materials for polymer electronic applications. In *Mater Res Soc Sym Proceed*; Cambridge Univ Press, 2003.
- 108. Wen, J., Wilkes, G. L. Organic/inorganic hybrid network materials by the sol-gel approach. *Chem Mater* 8:1667–81, 1996.
- 109. Etienne, P., Phalippou, J., Sempere, R. Mechanical properties of nanocomposite organosilicate films. *J Mater Sci* 33:3999–4005, 1998.
- Mackenzie, J. D., Huang, Q., Iwamoto, T. Mechanical properties of ormosils. J Sol-Gel Sci Technol 7:151–61, 1996.
- 111. Greiwe, K., Glaubitt, W., Amberg-Schwab, S., Piana, K. Characterisation of hydrolysed alkoxysilanes and zirconiumalkoxides for the development of UV-curable scratch resistant coatings. In *MRS proceed*; Cambridge Univ Press, 1992.
- 112. Amberg-Schwab, S., Weber, U., Burger, A., Nique, S., Xalter, R. Development of passive and active barrier coatings on the basis of inorganic-organic polymers. *Monatshefte für Chem* 137:657–66, 2006.
- 113. Jitianu, A., Klein, L. C. Sol-gel hybrids for electronic applications. In *Hybrid* Nanocomposites for Nanotechnology, Electronic, Optical, Magnetic and

*Biomedical Applications*, ed. L. Merhari, p. 448. New York, USA: Springer, 2009.

- 114. Marini, M., De Niederhausern, S., Iseppi, R., Bondi, M., Sabia, C., Toselli, M., et al. Antibacterial activity of plastics coated with silver-doped organic-inorganic hybrid coatings prepared by sol-gel processes. *Biomacromol* 8:1246– 54, 2007.
- 115. Tonnie, A. A Reference Searching Related to Nanomaterials, Food Packaging and Sustainability. 2007.
- Hussain, F., Hojjati, M., Okamoto, M., Gorga, R. E. Review article: Polymermatrix nanocomposites, processing, manufacturing, and application: An overview. J Compos Mater 40:1511–75, 2006.
- 117. Wu, C. L., Zhang, M. Q., Rong, M. Z., Friedrich, K. Tensile performance improvement of low nanoparticles filled-polypropylene composites. *Compos Sci Technol* 62:1327–40, 2002.
- 118. Vladimirov, V., Betchev, C., Vassiliou, A., Papageorgiou, G., Bikiaris, D. Dynamic mechanical and morphological studies of isotactic polypropylene/ fumed silica nanocomposites with enhanced gas barrier properties. *Compos Sci Technol* 66:2935–44, 2006.
- 119. Tang, S., Zou, P., Xiong, H., Tang, H. Effect of nano-SiO<sub>2</sub> on the performance of starch/polyvinyl alcohol blend films. *Carbohydr Polym* 72(3):521–6, 2008.
- 120. Jia, X., Li, Y., Cheng, Q., Zhang, S., Zhang, B. Preparation and properties of poly (vinyl alcohol)/silica nanocomposites derived from copolymerization of vinyl silica nanoparticles and vinyl acetate. *Eur Polym J* 43:1123–31, 2007.
- 121. Zhou, X., Shin, E., Wang, K., Bakis, C. Interfacial damping characteristics of carbon nanotube-based composites. *Compos Sci Technol* 64:2425–37, 2004.
- 122. Bin, Y., Mine, M., Koganemaru, A., Jiang, X., Matsuo, M. Morphology and mechanical and electrical properties of oriented PVA–VGCF and PVA–MWNT composites. *Polymer* 47:1308–17, 2006.
- 123. Zeng, H., Gao, C., Wang, Y., Watts, P. C., Kong, H., Cui, X., et al. In situ polymerization approach to multiwalled carbon nanotubes-reinforced nylon 1010 composites: Mechanical properties and crystallization behavior. *Polymer* 47:113–22, 2006.
- 124. Morlat-Therias, S., Fanton, E., Gardette, J., Peeterbroeck, S., Alexandre, M., Dubois, P. Polymer/carbon nanotube nanocomposites: Influence of carbon nanotubes on EVA photodegradation. *Polym Degrad Stab* 92:1873–82, 2007.
- 125. Prashantha, K., Soulestin, J., Lacrampe, M., Krawczak, P., Dupin, G., Claes, M. Masterbatch-based multi-walled carbon nanotube filled polypropylene nanocomposites: Assessment of rheological and mechanical properties. *Compos Sci Technol* 69:1756–63, 2009.
- 126. Kim, J. Y., Han, S. I., Kim, D. K., Kim, S. H. Mechanical reinforcement and crystallization behavior of poly (ethylene 2, 6-naphthalate) nanocomposites induced by modified carbon nanotube. *Compos Part A: Appl Sci Manufact* 40:45–53, 2009.

- 127. Wakabayashi, K., Pierre, C., Dikin, D. A., Ruoff, R. S., Ramanathan, T., Brinson, L. C., *et al.* Polymer-graphite nanocomposites: Effective dispersion and major property enhancement via solid-state shear pulverization. *Macromol* 41:1905–8, 2008.
- Borriello, C., De Maria, A., Jovic, N., Montone, A., Schwarz, M., Antisari, M. V. Mechanochemical exfoliation of graphite and its polyvinyl alcohol nanocomposites with enhanced barrier properties. *Mater Manufact Processes* 24:1053–7, 2009.
- 129. Sinha Ray, S. Polylactide-based bionanocomposites: A promising class of hybrid materials. *Acc Chem Res* 45:1710–20, 2012.
- 130. Ray, S., Quek, S. Y., Easteal, A., Chen, X. D. The potential use of polymerclay nanocomposites in food packaging. *International Journal of Food Engineering*. 2:1, 2006.
- Sorrentino, A., Gorrasi, G., Vittoria, V. Potential perspectives of bio-nanocomposites for food packaging applications. *Trends Food Sci Technol* 18:84– 95, 2007.
- Ray, S. S., Yamada, K., Ogami, A., Okamoto, M., Ueda, K. New polylactide/ layered silicate nanocomposite: Nanoscale control over multiple properties. *Macromol Rapid Commun* 23:943–7, 2002.
- Paul, D., Robeson, L. Polymer nanotechnology: Nanocomposites. *Polymer* 49:3187–204, 2008.
- 134. Sinha Ray, S., Yamada, K., Okamoto, M., Ueda, K. Polylactide-layered silicate nanocomposite: A novel biodegradable material. *Nano Lett* 2:1093–6, 2002.
- 135. Silvestre, C., Duraccio, D., Cimmino, S. Food packaging based on polymer nanomaterials. *Progs Polym Sci* 36:1766–82, 2011.
- Uyama, H., Kuwabara, M., Tsujimoto, T., Nakano, M., Usuki, A., Kobayashi, S. Green nanocomposites from renewable resources: Plant oil-clay hybrid materials. *Chem Mater* 15:2492–4, 2003.
- 137. Soulestin, J., Rashmi, B. J., Bourbigot, S., Lacrampe, M., Krawczak, P. Mechanical and optical properties of polyamide 6/clay nanocomposite cast films: Influence of the degree of exfoliation. *Macromol Mater Eng* 297:444– 54, 2012.
- 138. Demetrakakes, P. Nanocomposites raise barriers http://www.findarticles. com, 2002.
- 139. Fornes, T., Paul, D. Modeling properties of nylon 6/clay nanocomposites using composite theories. *Polymer* 44:4993–5013, 2003.
- 140. Arora, A., Padua, G. Review: Nanocomposites in food packaging. *J Food Sci* 75:R43–9, 2010.
- 141. Okada, A., Kawasumi, M., Usuki, A., Kojima, Y., Kurauchi, T., Kamigaito, O. Nylon 6-clay hybrid. In *MRS proceed*; Cambridge Univ Press, 1989.
- 142. Lan, T., Pinnavaia, T. J. Clay-reinforced epoxy nanocomposites. *Chem Mater* 6:2216–9, 1994.
- 143. Cabedo, L., Giménez, E., Lagaron, J. M., Gavara, R., Saura, J. J. Development of EVOH-kaolinite nanocomposites. *Polymer* 45:5233–8, 2004.

- 144. Petersson, L., Oksman, K. Biopolymer based nanocomposites: Comparing layered silicates and microcrystalline cellulose as nanoreinforcement. *Compos Sci Technol* 66:2187–96, 2006.
- 145. Yu, Y., Lin, C., Yeh, J., Lin, W. Preparation and properties of poly (vinyl alcohol)-clay nanocomposite materials. *Polymer* 44:3553–60, 2003.
- 146. Bertini, F., Canetti, M., Audisio, G., Costa, G., Falqui, L. Characterization and thermal degradation of polypropylene–montmorillonite nanocomposites. *Polym Degrad Stab* 91:600–5, 2006.
- 147. Cyras, V. P., Manfredi, L. B., Ton-That, M., Vázquez, A. Physical and mechanical properties of thermoplastic starch/montmorillonite nanocomposite films. *Carbohydr Polym* 73:55–63, 2008.
- 148. Weiss, J., Takhistov, P., McClements, D. J. Functional materials in food nanotechnology. *J Food Sci* 71:R107–16, 2006.
- Ramanathan, T., Abdala, A., Stankovich, S., Dikin, D., Herrera-Alonso, M., Piner, R., *et al.* Functionalized graphene sheets for polymer nanocomposites. *Nature Nanotechnol* 3:327–31, 2008.
- 150. Althues, H., Henle, J., Kaskel, S. Functional inorganic nanofillers for transparent polymers. *Chem Soc Rev* 36:1454–65, 2007.
- Roe, D., Karandikar, B., Bonn-Savage, N., Gibbins, B., Roullet, J. Antimicrobial surface functionalization of plastic catheters by silver nanoparticles. J Antimicrob Chemother 61:869–76, 2008.
- 152. Silvestre, C., Cimmino, S., Raimo, M., Duraccio, D., del Amo Fernandez, B., Lafuente, P., *et al.* Structure and morphology development in films of mLL-DPE/LDPE blends during blowing. *Macromol Mater Eng* 291 (12): 1477–85, 2006.
- Kumar, R., Münstedt, H. Silver ion release from antimicrobial polyamide/ silver composites. *Biomater* 26:2081–8, 2005.
- 154. Liau, S., Read, D., Pugh, W., Furr, J., Russell, A. Interaction of silver nitrate with readily identifiable groups: Relationship to the antibacterialaction of silver ions. *Lett Appl Microbiol* 25:279–83, 1997.
- 155. Damm, C., Münstedt, H., Rösch, A. The antimicrobial efficacy of polyamide 6/silver-nano-and microcomposites. *Mater Chem Phys* 108:61–6, 2008.
- 156. Damm, C., Münstedt, H., Rösch, A. Long-term antimicrobial polyamide 6/ silver-nanocomposites. *J Mater Sci* 42:6067–73, 2007.
- 157. Tankhiwale, R., Bajpai, S. Graft copolymerization onto cellulose-based filter paper and its further development as silver nanoparticles loaded antibacterial food-packaging material. *Colloids Surf B: Biointerface* 69:164–8, 2009.
- 158. Rhim, J., Hong, S., Park, H., Ng, P. K. Preparation and characterization of chitosan-based nanocomposite films with antimicrobial activity. *J Agric Food Chem* 54:5814–22, 2006.
- Hong, K. H., Park, J. L, Sul, I. H., Youk, J. H., Kang, T. J. Preparation of antimicrobial poly (vinyl alcohol) nanofibers containing silver nanoparticles. J Polym Sci Part B: Polym Phys 44:2468–74, 2006.

- 320 FUNCTIONAL POLYMERS IN FOOD SCIENCE
- 160. Rhim, J., Park, H., Ha, C. Bio-nanocomposites for food packaging applications. *Prog Polym Sci* 38:1629–52, 2013.
- Mbhele, Z., Salemane, M., Van Sittert, C., Nedeljkovic, J., Djokovic, V., Luyt, A. Fabrication and characterization of silver-polyvinyl alcohol nanocomposites. *Chem Mater* 15:5019–24, 2003.
- 162. Vermeiren, L., Devlieghere, F., Debevere, J. Effectiveness of some recent antimicrobial packaging concepts. *Food Addit Contam* 19:163–71, 2002.
- 163. Yoon, K., Hoon Byeon, J., Park, J., Hwang, J. Susceptibility constants of escherichia coli and bacillus subtilis to silver and copper nanoparticles. *Sci Total Environ* 373:572–5, 2007.
- Yoon, K. Y., Byeon, J. H., Park, C. W., Hwang, J. Antimicrobial effect of silver particles on bacterial contamination of activated carbon fibers. *Environ Sci Technol* 42:1251–5, 2008.
- 165. Kang, S., Mauter, M. S., Elimelech, M. Microbial cytotoxicity of carbonbased nanomaterials: Implications for river water and wastewater effluent. *Environ Sci Technol* 43:2648–53, 2009.
- 166. Cerrada, M. L., Serrano, C., Sánchez-Chaves, M., Fernández-García, M., Fernández-Martín, F., de Andres, A., *et al.* Self-Sterilized EVOH-TiO<sub>2</sub> nanocomposites: Interface effects on biocidal properties. *Adv Funct Mater* 18:1949–60, 2008.
- 167. Chawengkijwanich, C., Hayata, Y. Development of TiO 2 powder-coated food packaging film and its ability to inactivate escherichia coli in vitro and in actual tests. *Int J Food Microbiol* 123:288–92, 2008.
- Cheng, Q., Li, C., Pavlinek, V., Saha, P., Wang, H. Surface-modified antibacterial TiO 2/Ag + nanoparticles: Preparation and properties. *Appl Surf Sci* 252:4154–60, 2006.
- Wu, T., Wang, K., Li, G., Sun, S., Sun, J., Chen, J. Montmorillonite-supported ag/TiO2 nanoparticles: An efficient visible-light bacteria photodegradation material. ACS Applied Mater & interfaces 2:544–50, 2010.
- 170. Barnard, A. S. One-to-one comparison of sunscreen efficacy, aesthetics and potential nanotoxicity. *Nature Nanotechnol* 5:271–4, 2010.
- 171. Stoimenov, P. K., Klinger, R. L., Marchin, G. L., Klabunde, K. J. Metal oxide nanoparticles as bactericidal agents. *Langmuir* 18:6679–86, 2002.
- 172. Huang, L., Li, D., Evans, D., Duan, X. Preparation of highly dispersed MgO and its bactericidal properties. *The European Physical Journal D-Atomic, Molecular, Opt Plasma Phys* 34:321–3, 2005.
- Cioffi, N., Torsi, L., Ditaranto, N., Tantillo, G., Ghibelli, L., Sabbatini, L., *et al.* Copper nanoparticle/polymer composites with antifungal and bacteriostatic properties. *Chem Mater* 17:5255–62, 2005.
- 174. Mary, G., Bajpai, S., Chand, N. Copper (II) ions and copper nanoparticlesloaded chemically modified cotton cellulose fibers with fair antibacterial properties. *J Appl Plym* 113:757–66, 2009.

- 175. Tam, K., Djurišić, A., Chan, C., Xi, Y., Tse, C., Leung, Y., *et al.* Antibacterial activity of ZnO nanorods prepared by a hydrothermal method. *Thin Solid Films* 516:6167–74, 2008.
- 176. Droval, G., Aranberri, I., Germán, L., Ivanov, E., Dimitrova, E., Kotsilkova, R., *et al.* Thermal and rheological characterization of antibacterial nanocomposites poly (amide) 6 and low-density poly (ethylene) filled with zinc oxide. *J Thermoplast Compos Mater* 27:268–84, 2014.
- 177. Jones, N., Ray, B., Ranjit, K. T., Manna, A. C. Antibacterial activity of ZnO nanoparticle suspensions on a broad spectrum of microorganisms. *FEMS Microbiol Lett* 279:71–6, 2008.
- 178. Kerry, J., O'Grady, M., Hogan, S. Past, current and potential utilisation of active and intelligent packaging systems for meat and muscle-based products: A review. *Meat Sci* 74:113–30, 2006.
- 179. Fujishima, A., Rao, T. N., Tryk, D. A. Titanium dioxide photocatalysis. Journal of Photochemistry and Photobiology C: Photochem Rev 1:1–21, 2000.
- Li, H., Li, F., Wang, L., Sheng, J., Xin, Z., Zhao, L., *et al.* Effect of nano-packing on preservation quality of Chinese jujube. *Food Chem* 114:547–52, 2009.
- 181. Bouwmeester, H., Dekkers, S., Noordam, M. Y., Hagens, W. I., Bulder, A. S., De Heer C., *et al.* Review of health safety aspects of nanotechnologies in food production. *Regul Toxicol Pharm* 53:52–62, 2009.
- 182. Lee, S., Mao, C., Flynn, C. E., Belcher, A. M. Ordering of quantum dots using genetically engineered viruses. *Sciences* 296:892–5, 2002.
- 183. Ai, K., Liu, Y., Lu, L. Hydrogen-bonding recognition-induced color change of gold nanoparticles for visual detection of melamine in raw milk and infant formula. J Am Chem Soc 131:9496–7, 2009.
- Mills, A., Hazafy, D. Nanocrystalline SnO 2-based, UVB-activated, colourimetric oxygen indicator. Sens Actuators B: Chem 136:344–9, 2009.
- 185. Jurmanović, S., Kordić, Š., Steinberg, M. D., Steinberg, I. M. Organically modified silicate thin films doped with colourimetric pH indicators methyl red and bromocresol green as pH responsive sol-gel hybrid materials. *Thin Solid Films* 518:2234–40, 2010.
- 186. Comini, E., Faglia, G., Sberveglieri, G., Calestani, D., Zanotti, L., Zha, M. Tin oxide nanobelts electrical and sensing properties. *Sens Actuators B: Chem* 111:2–6, 2005.
- Comini, E., Faglia, G., Sberveglieri, G., Zanotti, L. Oxide nanobelts as conductometric gas sensors. *Mater Manufact Processes* 21:229–32, 2006.
- 188. Pimtong-Ngam, Y., Jiemsirilers, S., Supothina, S. Preparation of tungsten oxide-tin oxide nanocomposites and their ethylene sensing characteristics. *Sens Actuators A: Phys* 139:7–11, 2007.
- Kaushik, A., Solanki, P. R., Pandey, M., Ahmad, S., Malhotra, B. D. Cerium oxide-chitosan based nanobiocomposite for food borne mycotoxin detection. *Appl Phys Lett* 95:173703, 2009.
- 190. Mo, Z., Zhang, Y., Zhao, F., Xiao, F., Guo, G., Zeng, B. Sensitive voltammetric determination of sudan I in food samples by using gemini surfactant-ionic

liquid-multiwalled carbon nanotube composite film modified glassy carbon electrodes. *Food Chem* 2010;121:233–7.

- 191. Wei, D., Bailey, M. J., Andrew, P., Ryhänen, T. Electrochemical biosensors at the nanoscale. *Lab on a Chip* 9:2123–31, 2009.
- 192. Bordes, P., Pollet, E., Avérous, L. Nano-biocomposites: Biodegradable polyester/nanoclay systems. *Prog Polym Sci* 34:125–55, 2009.
- 193. Pandey, J. K., Kumar, A. P., Misra, M., Mohanty, A. K., Drzal, L. T., Palsingh, R. Recent advances in biodegradable nanocomposites. *J Nanosci Nanotechnol* 5:497–526, 2005.
- 194. Sinha Ray, S., Bousmina, M. Biodegradable polymers and their layered silicate nanocomposites: In greening the 21st century materials world. *Prog Mater Sci* 50:962–1079, 2005.
- 195. Yang, K., Wang, X., Wang, Y. Progress in nanocomposite of biodegradable polymer. *J Ind Eng Chem* 13:485, 2007.
- Petersen, K., Væggemose Nielsen, P., Bertelsen, G., Lawther, M., Olsen, M. B., Nilsson, N. H., *et al.* Potential of biobased materials for food packaging. *Trends Food SciTechnol* 10:52–68, 1999.

# Antimicrobial Active Polymers in Food Packaging

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#### Abstract

In the last decades there has been a paradigm shift in food packaging. Nowadays it is not only expected that food packaging act as a protective food barrier; what is expected is that during the period of time that the package is in direct contact with food, it will have a positive effect over food quality, safety and shelf life, becoming "active packaging." Within the different active packaging systems, antimicrobial packaging has become the focus of great attention as it acts on the food surface where the microorganisms grow. In this chapter, a review of the different antimicrobial agents that are included in polymer matrix is presented, including the different mechanisms to include these antimicrobial agents in the polymer and their kinetic release.

Keywords: Antimicrobial packaging, food packaging, antimicrobial release

### 10.1 Introduction to Food Packaging

The main objective for the food industry is to increase food shelf life, maintain food quality, and enhance food safety. The nature of shelf life of foods depends on intrinsic and extrinsic factors [1]. Intrinsic factors include pH, water activity (aw), nutrient content, redox potential, respiratory rate, and biological structure; whereas extrinsic factors include storage temperature, relative humidity, and the surrounding gas composition. A number

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of nontraditional preservation techniques are being developed to satisfy consumer demand with regard to nutritional and sensory aspects of foods. Generally, foods are thermally processed by subjecting them to temperatures varying from 60 to 100°C for the duration of a few seconds to a minute in order to destroy vegetative microorganisms. During this period of treatment, a large amount of energy is transferred to the food. However, this energy can trigger unwanted reactions, leading to undesirable organoleptic and nutritional effects [2]. Ensuring food safety and at the same time meeting such demands as nutritional retention and quality attributes has resulted in increased interest in alternative preservation techniques to inactivate microorganisms and enzymes in foods. Food packaging appears to be an alternative food preservation technique.

During the period of time that the packaging is in direct contact with food, packaging not only acts to protect food, it can also produce a positive effect on the food quality, food safety and even increase food shelf life. Food packaging requires a good selection of the material and packaging system in order to maintain food quality and increase food shelf life. In order to select the best packaging system to ensure food shelf life, firstly, it is necessary to determine which are the main factors that determine product shelf life. Once the protection requirements of food are defined, it is also necessary to know the properties of the packaging material and the packaging system in order to combine these two elements.

Traditional packaging has focused its attention on the inertness between packaging and food product, diminishing natural interaction processes between packaging and food product (sorption, migration and permeation). The understanding of these mass transference processes has been one of the main issues in food packaging. In the last decades a new food packaging concept has arisen, the concept of an "active food packaging system," which is supposed to perform some other role than providing an inert barrier to external conditions. Active packaging (AP) system involves a positive interaction between the packaging material and the food in order to provide desirable effects and extend the shelf life of packaged foods. The food-package interaction is achieved by the addition of certain additives into the packaging film to enhance the performance of the packaging system [3]. In Europe, active packaging is governed by EU Regulations 1935/2004/EC and 450/2009/EC, and is described as "active food contact materials and articles" (herein after referred to as active materials and articles) means materials and articles that are intended to extend the shelf life or to maintain or improve the condition of packaged food. They are designed to deliberately incorporate components that would release or

absorb substances into or from the packaged food or the environment surrounding the food (European Commission Regulation (EC) 2009) [4,5].

Active and intelligent materials and articles may only be placed on the market if they meet the following conditions:

- a) They are suitable and effective for the intended purpose of use.
- b) They comply with the general requirements set out in Article 3 of Regulation (EC) No 1935/2004. Materials and articles, including active and intelligent materials and articles, shall be manufactured in compliance with good manufacturing practice so that, under normal or foreseeable conditions of use, they do not transfer their constituents to food in quantities which could: (i) endanger human health; or (ii) bring about an unacceptable change in the composition of the food; or (iii) bring about a deterioration in the organoleptic characteristics thereof.
- c) They comply with the special requirements set out in Article 4 of Regulation (EC) No 1935/2004. Active materials and articles may bring about changes in the composition or organoleptic characteristics of food on condition that the changes comply with the Community provisions applicable to food, such as the provisions of Directive 89/107/EEC on food additives and related implementing measures, or, if no Community provisions exist, with the national provisions applicable to food.
- d) They also must comply with the labeling requirements set out in Article 15(1)(e) of Regulation (EC) No 1935/2004; comply with the composition requirements Regulation (EC) No 1935/2004; and comply with labeling and declaration requirements set out Regulation (EC) No 1935/2004. In the case of active materials and articles, information on the permitted use or uses and other relevant information such as the name and quantity of the substances released by the active component so as to enable food business operators who use these materials and articles to comply with any other relevant Community provisions or, in their absence, national provisions applicable to food, including the provisions on food labeling.
- e) When the active action involves release of active components to food, these will be consider as ingredients and material

must not produce changes that mislead consumers as masking the spoilage of food. Although only substances listed in the Community list of permitted substances may be used in components of the active materials and articles, there is an exception for active substances release that must comply to national food regulations. The substances must not be mutagenic, carcinogenic or toxic for reproduction.

Active packaging techniques can be divided into three categories: absorbers, releasing systems and other systems. Scavenging systems remove undesired components such as oxygen, carbon dioxide, ethylene, and humidity. Releasing systems actively add or emit compounds to the packaged food or into the headspace of the package, such as carbon dioxide, antioxidants and preservatives. Other systems may have miscellaneous tasks such as self-heating, self-cooling and preservation [6].

Antimicrobial packaging is one of the most interesting and promising components of AP, which potentially allows industry to combine the preservative functions of antimicrobial (AM) agents with protective functions for foods, and is an alternative way to use antimicrobial agents for food safety. When the packaging material acquires antimicrobial activity, the packaging material limits or prevents microbial growth by reducing growth rate or by decreasing live counts of microorganisms [7,8]. When food-grade antimicrobial substances are incorporated into polymer, the use of antimicrobial films allows the release of active compounds from the film, and continuous antimicrobial effects take place on the food surface during the exposure time, increasing consumer safety because these compounds are included in the packaging structure instead of being directly added to food, and are released in smaller amounts on the food surface.

A wide range of antimicrobial substances have been tested in laboratories for their potential applications in antimicrobial food packaging. These substances include organic acids (benzoic acid, sorbates), enzymes (lysozyme, glucose oxidase), bacteriocins (nisin, pediocin), fungicides (benomyl, imazalil), polymers (predominantly chitosan), natural extracts, antibiotics, triclosan, and silver compounds. Each antimicrobial substance exhibits a unique mechanism of action that is specific to a particular range of foods and microorganisms. Some antimicrobials block or inhibit metabolic and reproductive processes of microorganisms, while others modify their cell wall conformation, leading to the loss of vital internal materials and adaptability in the medium. However, this point can be a disadvantage for antimicrobial food-packaging systems, since an antimicrobial film may have limited applicability in certain food products. From a commercial standpoint, this shortcoming may reduce marketing opportunities and potential applications [9].

### 10.2 Antimicrobial Agents

Many antimicrobial agents are widely used in the food, food packaging, aromatherapy, pharmaceuticals and cosmetic products. Each industry must respect the regulations of the industry sector and the country where they will be used. Antimicrobial agents (AM) encompass different activities and different microorganisms due to the characteristic antimicrobial mechanisms and the various physiologies of microorganisms.

A broad range of antimicrobials have received attention for antimicrobial food packaging developments; also taken into consideration is the requirement for the release elements to be nonintrusive, cheap, and compatible with the geometry and physicochemical properties of food. Whereas volatile antimicrobials (such as essential oils or their active components) have been proposed in the case of foods with a low mass/volume ratio (such as salads), water-soluble antimicrobials have been indicated as most appropriate when direct contact with the food is involved (for instance, meat and meat cuts).

An appropriate AM substance and its concentration, the microorganism to be attacked, the polymer matrix, the food (nature and pH), storage temperature and solubility of the agent into the polymer and on the food, are important parameters to take into account in the formulation of an active material. The chemical properties of the AM substance, such as solubility, are also important factors. The compatibility of the AM agent and the packaging material is one of the most important elements to be taken into account, being that the AM effectiveness inside the package is dependent on its interaction with the particular packaging material. The pH of the system is also crucial. Most of the AM substances alter their activity with the pH, which will be dependent on the pH of the packaged food composition. Moreover, it is important to maintain the physical and mechanical properties of packaging materials after the incorporation of the AM substances.

Antimicrobial agents can protect food through different mechanisms: i) they can be mixed with food ingredients; ii) they can be incorporated into packaging formulation; and iii) they can be immersed into package headspace atmosphere. In the case of a food additive and when it is added to the polymeric formulation with the purpose to be later released into the food, AM substances are controlled as food ingredients. Even when AM substances are additives of packaging materials, when their purpose is to be delivered into the food, they are required to be GRAS grade substance. Although a large number of chemicals have been described that show potential as food preservatives, only a relatively small number are allowed in food products, due in large part to the strict rules of safety adhered to by the Food and Drug Administration (FDA) and to a lesser extent to the fact that not all compounds that show antimicrobial activity *in vitro* do so when added to certain foods.

It is also necessary to conform to the regulatory legislation where the food package will be used. In the case of non-food-grade chemicals, the only way to be incorporated into the food packaging is by its immobilization through chemical binding of the antimicrobial compound to polymeric material. Anyway, it will be necessary to verify that no migration occurs.

Several published papers and reviews have already presented the most important types of antimicrobial agents and works related to them [10-12]. In this section, some of the most used and interesting antimicrobial agents are also described, some of which have already been used in the development of active materials for food packaging applications, and only the latest developments will be presented in Tables 10.1 and 10.2 as examples. Antimicrobial agents have been divided in four groups: natural substances, chemical agents, probiotics and polymers that present antimicrobial properties by themselves.

### 10.2.1 Natural Antimicrobial Agents

Natural antimicrobial substances include animal, microbial and plant origin antimicrobial agents. Many efforts have been scientifically expended to discover new antimicrobial compounds from various kinds of sources such as soil, microorganisms, animals and plants.

### 10.2.1.1 Bacteriocins

Bacteriocins are antimicrobial peptides produced by bacteria which kill or inhibit the growth of other similar bacterial strains. For instance, the known safe food-grade lactic acid bacteria (LAB) produces a variety of bacteriocins with desirable properties that make them suitable for food preservation, such as: i) they are generally recognized as safe substances (GRAS); ii) they are nontoxic and nonactive substances on eukaryotic cells; iii) they have little influence on the gut microbiota; and iv) they have

<b>Lable 10.1</b> Antimicrobials incorporated into polymers used for food protection.	incorporated 1	nto polymers used	a for 1000 protection.	
AM agent	Polymer	Food	Microorganism	Reference
Bacteriocins				
Nisin	PE	Beef	Carnobacterium spp. & others	La Storia et al., 2012 [95]
	РОИН	Sausage	Listeria monocytogenos	Marcos et al., 2013 [96]
Nisin & Natamycin	PVC	Cheese	Penicillium expansum, Fusarium cul- morum & others	Hanusova et al., 2010 [97]
	VDC/EVA	Beef	Brochotrix thermosphecta	Ercolini et al., 2010 [98]
Lactocin 75	LLDPE	Culture media	Listeria innocua	Blanco Massani et al., 2013 [99]
Antibiotics				
Natamycin	SPI/PLA	Tomato	E. coli, mold & others	Gonzalez & Alvarez Igarzabal, 2013 [27]
	chitosan	Cheese	A. niger	Fajardo et al., 2010 [28]
Enzymes				
Lysozyme	PET	Culture media	Micrococcus lysodeikticus	Corradini et al., 2013 [35]
Lysozyme & Lactoferrin	Cellullose	meat	L. innocua, E. coli	Barbiroli et al., 2012 [34]
Lactoperoxidase	chitosan	Culture media	Xanthanos campestris, Colletotridrum gloeosporioides & others	Mohamed et al., 2013 [38]
Organic acids and derivatives	S			
Sorbic acid	PVA	Cheese	E. coli, Saccharomyces cerevisiae & others	Hauser & Wunderlich, 2011 [54]

 Table 10.1
 Antimicrobials incorporated into polymers used for food protection.

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AM agent	Polymer	Food	Microorganism	Reference
Propionic acid	Corn zein	cereal	Sitophilus granarius	Germinara et al., 2010 [56]
	chitosan	pastry dough	Salmonella spp., Penicillium & others	Rivero et al., 2013 [55]
Benzoic & Sorbic acids	chitosan	Culture media	E. coli, Staphylococcus aureus & others	Cruz-Romero et al., 2013 [53]
Potassium sorbate	Wheat Gluten	Culture media	A. niger, F. incarnatum	Türe et al., 2012 [52]
Lactic acid	Polyamide	Beef	Enterobacteriacae, E. coli	Smulders et al., 2013 [52]
Other chemical agents				
LAE	EVOH	Infant formula	Salmonella enterica & others	Muriel-Galet et al., 2012 [63]
	chitosan	Chicken	Listeria monocytogenes, E. coli & others	Higueras et al., 2013 [64]
AIT	Paper		Penicillium expansum, Escherichia coli, Listeria monocytogenes	Piercey et al., 2012 [78]
Probiotics Lactobacillus reuteri	Alginate	Sausages	Pediococcus pentosaceus, Staphylococcus carnosus	Muthukumarasamy & Holley, 2006 [82]
Lactobacillus curvatus CRL705	1	Beef	Brochothrix thermosphacta & others	Castellano et al., 2013 [80]
AM polymer				
Chitosan	PET	Meat	Salmonella enterica, Campylobacter spp., Candida albicans & others	Zemljic et al., 2013 [100]
	chitosan	Fish soup	Listeria monocytogenes, Salmonella enterica, Staphylococcus aureus	Fernandez-Saiz et. al., 2010 [85]
	chitosan	Fresh vegetables	Staphylococcus aureus	Pitak & Rakshit, 2011 [101]

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<b>1able 10.2</b> Active materials based on natural antimicrobial agents from plants.	terials dased on na	itural antimicrobial a	agents from plants.	
AM agent	Polymer	Food	Microorganism	Reference
ESSENTIAL OILS (EO)				
Cinnamon EO	PET	Culture media	Aspergillus flavus	Manso <i>et al.</i> , 2013 [102]
Clove EO	Sunflower protein	Fish patties	Salmonella Cholerasuis Listeria innocua & others	Salgado <i>et al.</i> , 2013 [103]
Oregano EO	PP/EVOH	Salad	Enterobacteria Psychrotrophic Yeasts, molds & others	Muriel-Galet <i>et al.</i> , 2013 [63]
Lemon grass EO	gelatin	Sea bass	Enterobacteria Lactic acid bacteria	Ahmad <i>et al.</i> , 2012 [104]
PLANT EXTRACTS				
Mint extract and promegranate peel extract	Chitosan / PVOH	Culture media	Staphylococcus aureus Bacillus cereus	Kanatt <i>et al.</i> , 2012 [105]
Cocoa extract	EVOH	Milk	Staphylococcus aureus L. monocytogenes S. enterica E. coli	Calatayud <i>et al.</i> , 2013 [106]
Green tea extract	Chitosan	Pork sausages	Yeast and mold Lactic acid bacteria	Siripatrawan & Naipha, 2012 [107]

 Table 10.2
 Active materials based on natural antimicrobial agents from plants.

a broad antimicrobial spectrum against many foodborne pathogenic bacteria [13–15].

Though these bacteriocins are produced by LAB, nisin is currently the only bacteriocin widely used as a food preservative [16,17]. Nisin is a hydrophobic protein very effective against a wide range of spoilage and hazardous Gram-positive bacteria, such as *Lysteria monocytogenes*, and it is a very interesting AM compound to be incorporated in a polymeric material for food protection due to its high stability to moderate thermal processing and acidic environments.

Nisin is also considered an antimicrobial peptide produced from *Lactococcus lactis* fermentation [18]. It is a positively charged antibiotic peptide that is able to bind to negatively charged cytoplasmic membranes. Nisin contains 34 amino acids and has a molecular weight of 3.4 kD, killing bacteria by forming pores on cell membranes, and can be used broadly in food. During the last few years, several developments have been based on the incorporation of nisin into different polymeric matrices intended for food protection (see Table 10.1).

Other examples of bacteriocins for potential use in food packaging material are bavaricin, brevicin, carnocin, lacticin, mesenteracin, pediocin, sakacin, lactocin 75 and subtilin [19–23].

#### 10.2.1.2 Antibiotics and Fungicides

Antibiotics are secondary metabolites produced by microorganisms that inhibit or kill a wide spectrum of other microorganisms. Most of the useful ones are produced by molds and bacteria of the genus *Streptomyces*, and a few by *Bacillus* and *Paenibacillus spp*.

Although the use of chemical preservatives in foods is not popular among many consumers, and the idea of employing antibiotics is even less popular, nisin and natamycin are the two antibiotics widely used in foods. Nisin was already explained before as a bacteriocin, and natamycin is the most common antibiotic employed in the food industry, especially in dairy products such as cheese, for the prevention of molds and yeast contamination. It is a fungicide, also known as pimaricin, and belongs to polyethylene antibiotics, produced by aerobic fermentation of *Streptomyces natalensis* and related species. In general, yeasts are less resistant (minimum inhibitory concentration below 5 ppm) than molds (minimum inhibitory concentration above 10 ppm). Natamycin is permitted as an antimycotic in surface and cheese treatments in 32 countries but its use as a general food additive is more limited. In the European Union, natamycin (designated as preservative E235) is allowed for surface treatment of hard, semi-hard, and semi-soft cheeses as well as dry sausages [24]. In 1964, the studies of Klis and coworkers already proved the enormous effectiveness of natamycin compared to sorbic acid and other compounds [25]. Its mechanism of action is believed to result from a binding of natamycin to sterol molecules in fungal cell membranes that alters the permeability of the membranes and thereby causes disruption of cell processes. Several recent works are based on the incorporation of natamycin on different polymers [26–28].

Fungicides are also common antimicrobial agents, they are biocidal chemical compounds or biological organisms used to kill or inhibit fungi or fungal spores such as Benomyl or Imazalil, or Enilconazole, fungicides widely used in agriculture, particularly in the growing of citrus fruits. Imazalil is a systemic imidazole fungicide used to control a wide range of fungi on fruit, vegetables, and ornamentals, including powdery mildew on cucumber and black spot on roses. As fungicides are not permitted as a direct food preservative, they cannot be mixed into food ingredients or added to food-contact packaging materials. In the case of a formulation of an antimicrobial material with a fungicide, it is completely necessary to immobilize this substance in the polymer matrix by chemical binding [29,30].

#### 10.2.1.3 Antimicrobial Peptides

Antimicrobial peptides are usually described as short-size gene-encoded polypeptide substances synthesized by ribosome. Antimicrobial peptides appear to be ubiquitous and multipotent components of the innate immune defense arsenal used by both prokaryotic and eukaryotic organisms. They show a great diversity of primary structures, being most commonly classified by the number of disulfide bridges and particular amino-acid composition. Many of the antimicrobial agents inherent to animals are in the form of antimicrobial peptides [18,31].

Nisin was the first antimicrobial peptide to be isolated from natural sources in the 1950s from lactic acid bacteria for potential use as food preservative. Later, several antimicrobial peptides, such as magainins, cecropins and defensins, were isolated from natural sources as well, such as plants, insects, crustaceans, amphibians, and marine organisms [32].

Even AM peptides can be a very interesting alternative; few studies are still based on the incorporation of these compounds as active agents on food packaging materials.

### 10.2.1.4 Enzymes

Antimicrobial enzymes are ubiquitous in nature, playing a significant role in the defense mechanisms of living organisms against infection by bacteria and fungi. Hydrolytic antimicrobial enzymes function by degrading key structural components of the cell walls of bacteria and/or fungi, whereas antimicrobial oxidoreductases exert their effects by the generation *in situ* of reactive molecules [33].

When the antimicrobial packaging is based on the immobilization of the antimicrobial substance through binding to the surface of the package, a molecular structure large enough to retain activity on the microbial cell wall is required even though bound to the plastic. Such agents are likely to be limited to enzymes or other antimicrobial proteins.

The potential of these enzymes in food preservation is still slightly extended, lysozyme and lactoperoxidase being the two most studied enzymes on antimicrobial food packaging applications.

Lysozyme (1,4-beta-N-acetylmuramidase, 14.4 KDa), is a hydrolytic enzyme that plays an important role in preventing bacterial infection, especially for Gram-positive bacteria. It is abundant in a number of secretions such as tears, saliva, human milk, and mucus, and large amounts can be found in egg white. Its antimicrobial activity relies on the ability of hydrolyzing the b-1,4 linkage between N-acetyl muramic acid and N-acetyl glucosamine present in peptidoglycan. Gram-positive bacteria are very susceptible to lysozyme, because their cell wall is made up of 90% peptidoglycan; in Gram-negatives, peptidoglycan counts only for 5 to 10% of the cell wall. Nevertheless, lysozyme can be effective against Gram-negative bacteria in the presence of membrane destabilizing agents such as detergents and chelators as EDTA or lactoferrin [34]. Antimicrobial packaging applications employing lysozyme as active agent have been studied by several authors over the last few years [34–36].

The lactoperoxidase system also has a strong antimicrobial activity against bacteria and fungi. A wide range of both Gram-positive and Gram-negative bacteria are inhibited by the lactoperoxidase system, and some studies based on the incorporation of lactoperoxidase into polymers have already been carried out [37–39].

### 10.2.1.5 Plant Origin Antimicrobial Agents: Essential Oils and Plant Extracts

The consumer's desire for natural ingredients and for chemical preservative-free foods, and their higher familiarity with plant origin compounds as in herbal medicine, has increased the popularity of these types of natural antimicrobial agents.

Essential oils and organic plant extracts are gaining increasing interest because of their relatively safe status, their wide acceptance by consumers, and their exploitation for potential multipurpose functional uses, due to their multiple biological effects, including antimicrobial and antifungal activities, antioxidant, antiallergic, antiplatelet, anti-inflammatory, antitumor, antiviral and therapeutical properties [40–42]. Furthermore, researchers have increased their interest in biologically active compounds isolated from plant species for the elimination of pathogenic microorganisms because of the resistance that they have developed to antibiotics.

Spices and herbs are the two most important sources of antimicrobial agents which are effective against several Gram-positive and Gramnegative bacteria as well as yeast and fungi. Essential oils (EO) can be obtained from various parts of the plant matter; for example, the leaves (oregano, rosemary, thyme, basil, marjoram), flowers or bulds (clove), bulbs (garlic and onion), seed (parsley, grape), fruits (cardamom, cocoa), grass, roots, wood, and others.

Owing to their molecular structures based mainly on the presence of olefinic double bonds and functional groups such as hydroxyl, aldehyde and esters, they are hydrophobic, soluble in alcohol, nonpolar or weakly polar solvents, waxes and oils; most are liquid and of lower density than water (sassafras, vetiver, cinnamon and clove essential oils being exceptions) and are readily oxidizable by light, heat and air.

Essential oils are composed of a mixture of different compounds such as phenolic compounds, terpenes, aliphatic alcohols, aldehydes, ketones, acids and flavonoids. Terpenoids are the most abundant and present both as sesquiterpenes and especially as monoterpenes. The biological activity of essential oils is due to these terpenoids, particularly monoterpenoid phenols, which possess numerous functional properties. The components of essential oils can be aromatic and aliphatic constituents, all characterized by low molecular weight. Due to the volatile character of their principal constituents, the main drawback could be the organoleptical alteration of the packaged food due to the chemicals released by the active package, the study of their effect on food's organoleptic properties is necessary [43–45].

The antimicrobial activity is due to the composition, structure and functional groups of the extracts and the oils. The extraction method depends on the type of botanical material used and it is one of the key points which determines the final quality of the essential oil and the plant extracts. Also, various extraction methods can be used such as distillation, supercritical fluid extraction, microwave-assisted extraction, rectification and steam extraction, effleurage, fractional distillation, percolation, etc. The chemical composition of the oil differs quantitatively and qualitatively according to the extraction technique [46,47].

Most of the natural extracts are approved as GRAS by the US Food and Drug Administration.

Antimicrobial agents from plant extracts and essential oils have been incorporated into a spectrum of natural and synthetic polymers already in use for food packaging applications (Table 10.2).

The main problems associated with the incorporation of EOs on polymer matrix are related to their very low thermal resistance. Different authors have been working on incorporating essential oils such as cinnamaldehyde, thymol or carvacrol through extrusion process; nevertheless they report losses reaching up 73% [48–50].

### 10.2.2 Chemical Antimicrobial Agents

### 10.2.2.1 Organic Acids: Salts and Anhydrides

Organic acids are natural constituents of many foods, and they can also be produced by some microorganisms, although currently most of them are produced by chemical synthesis or chemically modified from natural acids. They have been used for a long time as additives in food preservation, food contact substances and food contact material sanitizers. They show nonspecific AM properties against bacteria and fungi. Their AM activity depends on the dissociation constant pKa. These compounds are most active at the lowest pH values of foods and essentially ineffective at neutral values.

The most common chemical antimicrobial agents used by researchers are various organic acids such as benzoic and sorbic acid, alkyl esters of p-hydroxybenzoic acid (parabens), sorbates [51,52], sorbic acid [53,54], propionic acid and its derivatives [55,56], acetic acid and their salts such as sodium, calcium and potassium acetate which are commonly used in bread and other baked goods, lactic acid and their mixtures [57,58].

Many fatty acids and monoglycerides also present antimicrobial activity against Gram-positive bacteria and some yeast [59]. These lipophilic substances exhibit an inhibitory effect against *C. Botulinum* for instance, and glyceryl monolaurate is commonly used in cured meats and refrigerated and packaged fresh fish. Their mechanism of action is based on the generation of holes in cell microorganism membranes by their ability to facilitate the conduction of protons through the cell membranes.

### 10.2.2.2 Ethyl-N-Lauroyl-1-Arginate (LAE)

One promising antimicrobial agent that has been around during recent developments is Ethyl-N- $\alpha$ -dodecanoyl-L-arginate hydrochloride or ethyl-N-lauroyl-l-arginate·HCl, commonly known as LAE. Commercialized as a white powder or in solution, it is synthesized by reacting l-arginine·HCl, ethanol, tionyl chloride, sodium hydroxide, lauryl chloride and deionized water. Its high antimicrobial effectiveness results from its chemical structure and surfactant properties [60,61]. The antimicrobial properties of LAE are due to its action as cationic surfactant on cytoplasmic membrane and the outer membrane of Gram-negative, and cell membrane and cytoplasm of Gram-positive denaturation proteins. These changes produce disturbances in membrane potential, resulting in cell growth inhibition and loss of viability.

LAE is characterized by a broad spectrum and high antimicrobial efficiency against Gram-negatives, Gram-positives, fungi and yeasts, with a low-dose application. Furthermore, because it is primarily and rapidly metabolized and hydrolyzed chemically in the human body to natural endogenous compounds present in the human diet, having an important degree of security, it has been classified as GRAS (generally recognized as safe) and as a food additive by both the Food and Drug Administration (FDA) in 2005 and the European Food Safety Agency (EFSA) in 2007 and 2009. Because of all these reasons, LAE has become an interesting antimicrobial substance to be incorporated into active food packaging material. Some of the developments based on the incorporation of LAE into different polymer matrices are presented in Table 10.1 [62–64].

#### 10.2.2.3 Silver

Silver ions and nanoparticles are probably the metal particles most used as antimicrobial agent in polymeric nanocomposites because of their broad antimicrobial spectrum of action against bacteria, virus and fungi. Nevertheless, their mechanism of action is not yet clear. Silver in its metallic state can react with moisture to be ionized, releasing highly reactive Ag<sup>+</sup> ions. The ionized silver can bind to proteins causing structural changes in the cell wall and also in the nuclear membranes, provoking cell death. The Ag<sup>+</sup> ions also form complexes with bases contained in DNA and RNA, inhibiting the microorganism replication. Furthermore, several studies reported that the size and the shape of the silver nanoparticle influences the antimicrobial behavior, as well as its oxidation number, Ag<sup>0</sup> or Ag<sup>+</sup>, in the matrix. Moreover, there are diverse techniques to incorporate silver

into a polymeric matrix. One of them is through silver-substituted zeolites, which are widely used as polymer additives for food applications, especially in Japan. Silver ions are antimicrobial against a wide range of bacteria and molds. Silver zeolites have already been incorporated in polymers like polyethylene, polypropylene, and nylon at levels of 1–3% [65]. Several commercial applications have already been developed as Zeomic. In Japan, silver-substituted zeolite has been developed as the most common antimicrobial agent incorporated into plastics.

### 10.2.2.4 Copper

Copper has recently gained attention as an antimicrobial agent because of its inhibitory effects on bacteria, yeast, and viruses. It is common knowledge that microorganisms require low concentrations of copper ions as essential micronutrients and as vital cofactors for processing of metaloproteins and certain enzymes. Higher concentrations of copper (250 ppm) can cause inhibition of growth or even death of microorganisms. The toxic effect of copper on microorganisms occurs by the displacement of essential ions, thereby obstructing functional groups of proteins, inactivating enzymes, producing hydroperoxide free radicals, and altering membrane integrity [66]. Several works are related to the antimicrobial activity of copper, as nanoparticles and complexed as well [67–69].

Copper particles are also known for their antimicrobial activity, although they are relatively less studied than silver. Polypropylene (PP) nanocomposites containing different amounts of Cu nanoparticles were prepared by melt mixed method where composites with only 1% (v/v) of Cu were able to kill 99.9% of bacteria after 4 h of contact [70]. Moreover, nanocomposites of copper and polystyrene (PS) were synthesized in situ by the addition of Cu nanoparticles during the polymerization. They showed an important antibacterial activity tested against P. fluorescens, B. circulans, E. coli and S. aureus [71]. Antimicrobial nanocomposites with dual action based on copper have also been described. Cationic polyvinylpyrrolidone (PVP) polymeric particles were used for *in situ* Cu metal nanoparticle syntheses [72]. The bactericidal action was tested against S. aureus, P. aeruginosa, B. subtilis and E. coli. Although they showed antimicrobial activity, their minimal inhibitory concentration (MIC) values were higher than the composites of silver nanoparticles. Several studies are also focused on the incorporation of the copper nanoparticles at the surface of polymers. Copper ion implantation by plasma immersion was employed to create antibacterial surface on PEs, exhibiting excellent long-term antibacterial effects against E. coli

and S. aureus [73]. These properties were improved when gases such as  $\rm N_{_2}$  were plasma-implanted in concert with Cu [74,75].

#### 10.2.2.5 Other Chemical Agents

Antimicrobial chemical inorganic acids and their salts, sulfites, nitrites and alcohols are some of the chemical agents that have been broadly used for food preservation.

Sulfur dioxide (SO<sub>2</sub>) and its derivatives have been widely used as food preservatives. They are added to inhibit and control microorganisms' growth and enzymatic catalytic reactions. The commonly used forms in foods include SO<sub>2</sub> gas, and sodium, potassium or calcium salts of sulfite (SO<sub>3</sub><sup>2-</sup>), bisulfate (HSO<sub>3</sub><sup>-</sup>) or metabisulfite (S<sub>2</sub>O<sub>5</sub><sup>2-</sup>). Sulfur dioxide acts as a biocidal and biostatic agent, and is more active against bacteria than molds and yeasts. Furthermore, it is more effective against Gram-negative bacteria than Gram-positive bacteria, and it is known to also have antioxidant activity in a variety of food systems [76,77]. Nevertheless, even though it is known to be the most effective antimicrobial agent in controlling the decay of some fruits, recently their use in foods became regulated and subjected to rigorous restrictions.

Another antimicrobial agent with volatile character is allyl isothiocyanate (AIT) derived from mustard seed, and it is commonly used as a flavoring. It is largely insoluble in aqueous systems and reacts readily with peptides and proteins. Several studies have shown its antimicrobial activity for food protection, such as on tomatoes or fresh-cut vegetables. Some works are related to their encapsulation on cyclodextrins and natural gums to reduce its odor and taste, and control the release [78,79].

Potassium and sodium salts of nitrite and nitrate are also antimicrobials commonly used for meat preservation. Their mechanism of action is unknown, but it has been suggested that it is based on the reaction between nitrite and sulfhydryl groups generating compounds that are not metabolized by microorganisms.

#### 10.2.3 Probiotics

Lactic acid bacteria, as various microorganisms, produces bacteriocins and a nonpeptide growth inhibiting chemical with antioxidant activity. But they can afford antimicrobial activity by itself as well. The use of probiotics can effectively control the competitive undesirable microorganisms. Many traditional fermented food products contain antimicrobial probiotics, although nowadays the research into the use of probiotics in the development of antimicrobial active packaging is limited.

Lactic acid bacteria (LAB) is a GRAS substance and it is the prevalent microbiota during the current storage conditions of fresh meat, being one of the most interesting probiotics for future development. Some works have already shown interesting results, as the application of Lactobacillus curvatures CRL705 for beef protection, or its action in combination with EDTA as a chelator agent [80–82]. Nevertheless, research has to be continued because some studies have also shown some negative organoleptical and muscle structure changes on meat.

### 10.2.4 Polymers Inherently Antimicrobial

The packaging material can serve as a source of releasing antimicrobial agents, or even prevent the growth of microorganisms by presenting antimicrobial properties by itself, as in the case of chitosan, or polymers obtained through synthesis based on polymerization of antimicrobial monomers.

Naturally, in the case of chitosan and poly-L-lysine, both biopolymers have antimicrobial activity owing to their specific structure.

Chitosan is a linear polysaccharide composed of randomly distributed  $\beta$ -(1,4)-linked D-glucosamine (deacetylated unit) and N-acetyl-Dglucosamine (acetylated unit). It is is a polycationic biopolymer industrially produced by chemical deacetylation of chitin which is found in arthropod exoskeletons, although it can also be obtained directly from the cell walls of some plant-pathogenic fungi. Due to its unique biological characteristics, including biodegradability and nontoxicity, many applications have been found either alone or blended with other natural polymers (starch, gelatin, alginates) in the food, pharmaceutical, textile, agriculture, water treatment and cosmetics industries. Antimicrobial activity of chitosan has been demonstrated against many bacteria, yeasts and a wide range of fungi. It can also trigger defensive mechanisms in plants and fruit against infections caused by several pathogens. It has a broad spectrum of activity and high killing rate against Gram-positive and Gram-negative bacteria. Several works are related to the use of chitosan in the development of antimicrobial materials and nanocomposites as well [83-85].

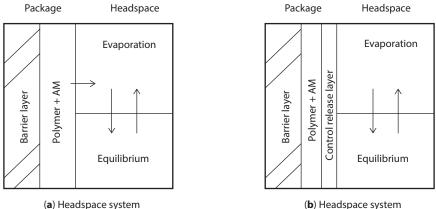
### 10.3 Antimicrobial Construction and Release System

Antimicrobial agents can be incorporated in a packaging system by different mechanisms. One of the mechanisms consists of including the AM agent in a sachet that can be incorporated inside the package [86]. In this case, the AM diffuses through the sachet, generating its antimicrobial action in the package headspace. Nevertheless, nowadays it is necessary to look for mechanisms in which the AM agent can be incorporated as a part of the packaging structure. This incorporation depends on the characteristics of the packaging material, antimicrobial agent and food.

The mechanism for the AM agent incorporation and its physical-chemical nature define the release mechanism of the AM agent. There are systems in which AM agents are released through a diffusion process; meanwhile when volatile AM agents are used they are released by evaporation into the headspace. Headspace antimicrobial agent concentration is then partitioned with the food product by an equilibrium sorption/isotherm. This system can also include a control layer release that controls the permeation of the volatile AM agent and maintains specific headspace concentration [87].

Furthermore, the AM agent can also be immobilized by being chemically bound to the packaging inner surface (Figure 10.1).

In both cases, the external barrier layer should be included in order to avoid the release of the AM agent outside the packaging. The AM agent can be incorporated through an extrusion process inside the polymer matrix



with control layer

Figure 10.1 Antimicrobial packaging system.

or by a coating process in the inner surface of the polymer matrix, in direct contact with food.

The design of AM packaging requires matching the release rate of the AM agents with the growth kinetics of the target microorganism, as it is necessary to maintain the concentration of the AM agent over the MIC on the food surface.

Depending on the food packaging system, the mechanism will change. The two main possible food packaging systems are presented below.

#### 10.3.1 Release System: Indirect Contact

Equilibrium of the AM substance among the headspace, polymeric material and the packaged food is taken into account as part of the main migration mechanism to calculate the real distribution of the AM agent.

In the case of a volatile substance that can migrate to the food and to the headspace package, equilibrium occurs between them as well.

The relationship between the sorption and the desorption of a volatile AM agent within a polymeric matrix is given in Equation 10.1:

$$\left[M_{t} / M_{\infty}\right]_{desorption} = 1 - \left[M_{t} / M_{\infty}\right]_{sorption}$$
(10.1)

where  $M_t$  is the total amount of a species that has migrated after time t, ad  $M_{\infty}$  is the maximum amount of the species that can migrate after an infinite time ( $t = \infty$ , namely, at equilibrium). The ration  $M_t/M_{\infty}$  is known as the fractional mass release. If the fractional mass release ratio is directly proportional to  $t_{1/2}$ , such a linearity would indicate compliance with the general law of diffusion [88], then the diffusion coefficient D (m<sup>2</sup> s<sup>-1</sup>) can be calculated by the half-time method according to Equation 10.2 [89]:

$$D = 0.0491 x L^2 / t_{0.5}$$
(10.2)

where *L* is the thickness of the film and  $t_{0.5}$  is the time required for 50% of the migrating species to be released into the food. Theoretical value of the fractional mass release as a function of time can be calculated assuming an exponential rise to a maximum level as indicated in Equation 10.3:

$$M_t / M_{\infty} = 1 - \exp(-kt)$$
 (10.3)

where *k* is the rate constant ( $s^{-1}$ ) that is dependent on the mass transfer properties, geometry and other conditions of the film material [49].

#### 10.3.2 Release Systems: Direct Contact

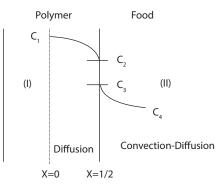
This is the case of a nonvolatile antimicrobial substance, which is necessary for direct contact between the package and food system, as the AM agent will migrate only through the contact area between the food and the material. The description of mass transfer in the migration processes through the plastic film can be achieved by means of Fick's law.

Figure 10.2 shows the main migration mechanism involved, based on these parameters: i) the diffusion between the packaging material and the food; ii) the partitioning coefficient of the interface. This figure represents the concentration profile of migrant compound through the plastic film (layer I), the distribution in the food phase in contact with the plastic package and the concentration profile through the boundary layer at the proximities of the interface (layer II). In migration analysis these profiles are symmetrical, considering the thickness according to the conditions of these tests. Thus, the mass transfer for this system can be explained by the resistances-in-series approach based on the one-dimensional simplification of Fick's Law.

From the system described in Figure 10.2, the instantaneous mass transfer of migrant compound by molecular diffusion through the plastic film may be estimated by Equation 9.4:

$$J_{I} = \frac{D_{p}}{L/2} (C_{1} - C_{2})$$
(10.4)

where  $J_1$  is the mass transfer flux (kg m<sup>-2</sup> s<sup>-1</sup>) of migrant compound through the polymer-food interface,  $D_p$  is the diffusion coefficient in the plastic film (m<sup>2</sup> s<sup>-1</sup>),  $C_1$  is the migrant concentration in the polymer bulk (kg m<sup>-3</sup>),  $C_2$ 



**Figure 10.2** Scheme of the migration process: concentration profiles and equilibrium conditions in the surrounding of the polymer/food interphase.

is the migrant concentration in the polymer side interface (kg m<sup>-3</sup>), and *L* is the film thickness (m). The dimensionless distribution coefficient of the migrant is represented by its concentration ratio between the polymer and the food phase ( $C_3$ ), respectively, in Equation 10.5:

$$K_{P/F} = \frac{C_2}{C_3}$$
(10.5)

Finally, the third step in the migration process is the transfer through the boundary layer in the food at the interface proximities, which can be described by Equation 10.6:

$$J_{II} = k \left( C_3 - C_4 \right) \tag{10.6}$$

where  $C_4$  is the migrant concentration in the food (kg m<sup>-3</sup>) and k is the mass transfer coefficient that quantify natural convection in food phase (m s<sup>-1</sup>). Equations 10.4 to 10.6 can be solved for an instantaneous time. In this case, the initial concentration of migrant in the polymer is considered from the following initial condition:

$$C_p^{(x,=)} = C_p^0 \tag{10.7}$$

Thus, if t = 0,  $C_1 = C_2 = C_p^{0}$ . On the other hand, no content of migrant in the food is considered at the beginning of the migration process, which defines a second initial condition:

$$C_F^{(x,0)} = 0 \tag{10.8}$$

This equation is involved if t = 0,  $C_3 = C_4 = 0$ . All calculations can be done in terms of the symmetrical conditions of the studied system, which is represented by Equation 9.9 as an additional border condition:

$$\left(\frac{\partial C_p^{(x,t)}}{\partial x}\right)_{x=0} = 0 \tag{10.9}$$

Taking into account that the initial concentration of migrant in the polymer and the bulk of the food are known, an iterative calculation can be done to estimate the mass transfer flux through the interface when  $J_I = J_{II}$  [90]. This calculation is necessary to determine if MIC is achieved on the food surface.

### 10.3.3 Non-release Systems

Non-release systems are when AM substances are covalently immobilized on polymeric surfaces and any type of mass transfer occurs.

### 10.3.3.1 Immobilization

Some antimicrobial packaging uses covalently immobilized non-foodgrade antimicrobial substances without diffusional mass transfer, such as packaging systems with covalently immobilized antibiotics or fungicides such as lisozyme or nisin [12,23].

### 10.3.3.2 Surface Modification

Surface modification is the introduction of chemical functional groups with AM activity into polymer films. Some cases are:

- New biopolymer containing a chito-oligosacharide side chain obtained through crosslinking of N-methylolacrylamide (NMA) on polyvinylacetate (PVA) [91].
- Surface amine groups formation in polymers through electron irradiation [92,93].
- Incorporation of anhydride linkages by reaction of acid/base treated films with benzoyl chloride [94].

## 10.4 Conclusions

Antimicrobial packaging is a new technology for the preservation of food that inhibits the growth of spoilage or pathogenic microorganisms, improving food quality, safety and shelf life. The design of antimicrobial packaging requires taking into account many factors such as characteristics of antimicrobial components, compatibility and interaction between antimicrobial agents and the packaging system, food nature and characteristics, target microorganisms, and compatibility of kinetics of the release of AM agent and growth kinetics of microorganisms.

# References

- 1. Pereira de Abreu, D. A., Cruz, J. M., Paseiro Losada, P. Active and Intelligent Packaging for the Food Industry. *Food Rev Int* 28:146-187, 2012.
- 2. Barbosa-Canovas, G. V., Pothakamury, U. H., Palou, E., Swanson, B. G. *Nonthermal Preservation of Foods*, p. 304. New York: Marcel Dekker, 1997.
- 3. Robertson, G. L. *Food packaging: Principles and Practice*, 2nd ed. London: CRC Press, 2006.
- European Commission Regulation (EC) No. 1935/2004 of the European Parliament and of the Council of 27 October 2004 on materials and articles intended to come into contact with food and repealing Directives 80/590/ EEC and 89/109/EEC. Official Journal of the European Union; 2004, L338/4.
- European Commission Regulation (EC) No. 450/2009 of 29 May 2009 on active and intelligent materials and articles intended to come into contact with food. Text with EEA relevance. *Official Journal of the European Union*; 2009, L135/3.
- 6. Ahvenainen, R. *Novel Food Packaging Techniques*. Woodhead Publishing Ld: Cambridge, England; 2003.
- 7. Galotto, M. J., Valenzuela, X., Rodriguez, F., Bruna, J., Guarda, A. Evaluation of the effectiveness of a new antimicrobial active packaging for fresh Atlantic Salmon (Salmon Salar L.) shelf life. *Packag Technol Sci* 25:363-372, 2012.
- 8. Mastromateo M., Danza A., Conte A., Muratore G., Del Nobile M. A. Shelf life of ready to use peeled shrimps as affected by thymol essential oil and modified atmosphere packaging. *Int J Food Microbiol* 144:250-256, 2012.
- 9. Han, J. H. Antimicrobial packaging systems. In *Innovations in Food Packaging*, ed. J. H. Han, p. 80. San Diego: Academic Press, 2005.
- 10. Han, J. H. Antimicrobial food packaging. Food Technol 54:56-65, 2000.
- 11. Suppakul, P., Miltz, J., Sonneveld, K., Bigger, S. W. Active packaging technologies with an emphasis on antimicrobial packaging and its applications. *J Food Sci* 68:408-420, 2003.
- 12. Appendini, P., Hotchkiss, J. H. Review of antimicrobial food packaging. *Innov Food Sci Emerg Tech* 3:113-126, 2002.
- 13. Barnby-Smith, FM. Bacteriocins: Applications in food preservation. *Trends Food Sci Tech* 3:133-137, 1992.
- 14. Gálvez, A., Abriouel, H., López, R. L., Omar, N. O. Bacteriocin-based strategies for food biopreservation. *Int J Food Microbiol* 120:51-70, 2007.
- 15. Cleveland J., Montville, T., Nes, I. F., Chikindas, M. L. Bacteriocins: Safe, natural antimicrobials for food preservation. *Int J Food Microbiol* 71:1-20, 2001.
- Delves-Broughton, J. Nisin, natamycin and other commercial fermentates used in food biopreservation. In. Protective Cultures, Antimicrobial Metabolites and Bacteriophages for Food and Beverage Biopreservation, ed. C. Lacroix. Woodhead, 2011.

- 17. Yildirim, S. Active packaging for food biopreservation. In *Protective Cultures, Antimicrobial Metabolites and Bacteriophages for Food and Beverage Biopreservation*, ed. C. Lacroix. Woodhead, 2011.
- Bi, L., Yang, L., Narsimhan, G., Bhunia, A. K., Yao, Y. Designing carbohydrate nanoparticles for prolonged efficacy of antimicrobial peptide. *J Controlled Release* 150:150-156, 2011.
- Blanco Massani, M., Vignolo, G. M., Eisenberga, P., Morando, P. J. Adsorption of the bacteriocins produced by Lactobacillus curvatus CRL705 on a multilayer-LLDPE film for food-packaging applications. *LWT-Food Sci Technol* 53:128-138, 2013.
- An, D., Kim, Y. M., Lee, S. B., Paik, H. D., Lee, D. S. Antimicrobial low density polyethylene film coated with bacteriocins in binder medium. *Food Sci Biotechnol* 9:14-20, 2000.
- 21. Luck, E., Jager, M. Antimicrobial Food Additives: Characteristic, Uses, Effects. Berlin: Springer, 1997.
- Natrajan, N., Sheldon, B. W. Efficacy of nisin coated polymer films to inactivate Salmonella typhimurium on fresh broiler skin. *J Food Protect* 63:1189-96, 2000.
- Scanell, A., Hill, C., Ross, R., Marx, S., Hartmeier, W., Arendt, E. Development of bioactive food packaging materials using immobilized bacteriocins lacticin 3147 and Nisaplin. *Int J Food Microbiol* 60:241-249, 2000.
- 24. European Commission Directive EC No 95/2 of 20 February 1995 on food additives other than colors and sweeteners. *Official Journal of European Communities* 1995; L6.
- Klis, J. B., Witter, L. D., Ordal, Z. J. The effect of several antifungal antibiotics on the growth of common food spoilage fungi. *Food Technol* 13:124–128, 1964.
- Krause Bierhalz, A. C., Altenhofen da Silva, M., Guenter Kieckbusch, T. Natamycin release from alginate/pectin films for food packaging applications. *J Food Eng* 110:18–25, 2012.
- 27. González, A., Alvarez-Igarzabal, C. I. Soy protein e Poly (lactic acid) bilayer films as biodegradable material for active food packaging. *Food Hydrocolloids* 33:289-296, 2013.
- Fajardo, P., Martins, J. T., Fuciños, C., Pastrana, L., Teixeira, J. A., Vicente, AA. Evaluation of a chitosan-based edible film as carrier of natamycin to improve the storability of Saloio cheese. *J Food Eng* 101:349–356, 2010.
- 29. Weng, Y. M. Development and application of food packaging films containing antimicrobial agents, PhD. Thesis, Food Science, Cornell University, 1992.
- Weng, Y. M., Hotchkiss, J. H. Inhibition of surface molds on cheese by polyethylene film containing the antimycotic imazalil. *J Food Prot* 55:367-369, 1992.

- 31. Wang, G. Antimicrobial peptides: Discovery, design & novel therapeutic strategies. In *Advances in Molecular and Celular Microbiology*, ed. G. Wang. Nebraska, 2010.
- Wang, H., Ran, R., Yu, H., Yu, Z., Hu, Y., Zheng, H., Wang, D., Yang, F., Liu, R., Liu, J. Identification and characterization of antimicrobial peptides from skin of Amolops ricketti (Anura Ranidae). *Peptides* 33:27-34, 2012.
- Thallinger, B., Prasetyo, E. N., Nyanhongo, G. S., Guebitz, G. M. Antimicrobial enzymes: An emerging strategy to fight microbes and microbial biofilms. *Biotechnol J* 8:97-109, 2013.
- Barbiroli, A., Bonomi, F., Capretti, G., Iametti, S., Manzoni, M., Piergiovanni, L., Rollini, M. Antimicrobial activity of lysozyme and lactoferrin incorporated in cellulose-based food packaging. *Food Control* 26:387-392, 2012.
- Corradini, C., Alfieri, I., Cavazzaa, A., Lantano, C., Lorenzi, A., Zucchetto, N., Montenero, A. Antimicrobial films containing lysozyme for active packaging obtained by sol–gel technique. *J Food Eng* 119:580-587, 2013.
- Mastromatteo, M., Lecce, L., De Vietro, N., Faviac, P., Del Nobile, M. A. Plasma deposition processes from acrylic/methane on natural fibres to control the kinetic release of lysozyme from PVOH monolayer film. *J Food Eng* 104:373-379, 2011.
- Lee, H., Min, S. C. Antimicrobial edible defatted soybean meal-based films incorporating the lactoperoxidase system. *LWT– Food Sci Technol* 54:42-50, 2013.
- Mohamed, C., Clementine, K. A., Didier, M., Gérard, L., Noëlle, D. M. Antimicrobial and physical properties of edible chitosan films enhanced by lactoperoxidase system. *Food Hydrocolloids* 30:576-580, 2013.
- Mecitoglu, C., Yemenicioglu, A. Partial purification and preparation of bovine lactoperoxidase and characterization of kinetic properties of its immobilized form incorporated into cross-linked alginate films. *Food Chem* 104:726-733, 2007.
- Chen, H., Yang, Y., Xue, J., Wei, J., Zhang, Z., Chen, H. Comparison of compositions and antimicrobial activities of essential oils from chemically stimulated agarwood, wild agarwood and healthy Aquilaria sinensis (Lour.) gilg trees. *Molecules* 14:4884-96, 2011.
- Djilani, A., Dicko, A. Chapter 7: The therapeutic benefits of essential oils. In Nutrition, Well-Being and Health, eds. J. Bouayed, T. Bohn. 2012.
- 42. Kordali, S., Kotan, R., Mavi, A., Cakir, A., Ala, A., Yildirim, A. Determination of the chemical composition and antioxidant activity of the essential oil of Artemisia dracunculus and of the antifungal and antibacterial activities of Turkish Artemisia absinthium, A. dracunculus, Artemisia santonicum, and Artemisia spicigera essential oils. J Agric Food Chem 30:9452-9458, 2005.
- Sadaka, F., Nguimjeu, C., Brachais, C., Vroman, I., Tighzert, L., Couvercelle, J. Review on antimicrobial packaging containing essential oils and their active biomolecules. *Innov Food Sci Emerg Technol* 2013; DOI: 10.1016/j. ifset.2013.01.004.

- 44. Tiwari, B. K., Valdramidis, V. P., O'Donnell, C. P., Muthukumarappan, K., Bourke, P., Cullen, P. J. Application of natural antimicrobials for food preservation. *J Agric Food Chem* 57:5987-6000, 2009.
- 45. Vidal, L., Avello, M., Loyola, C., Campos, J., Aqueveque, P., Dungan, S. R., Galotto, M., Guarda, A. Microencapsulation of maqui (Aristotelia chilensis-Molina Stuntz) leaf extracts to preserve and control antioxidant properties. *Chilean J Agric Res* 73:17-23, 2013.
- 46. Zhang, L. G., Zhang, C., Nia, L. J., Yang, Y. J., Wang, C. M. Rectification extraction of Chinese herbs' volatile oils and comparison with conventional steam distillation. *Sep Purif Technol* 77:261–268, 2011.
- 47. Shirsatha, S. R., Sonawanea, S. H., Gogate, P. R. Intensification of extraction of natural products using ultrasonic irradiations: A review of current status. *Chem Eng Proc* 53:10–23, 2012.
- Quintero, R. I., Galotto, M. J., Rodriguez, F., Guarda, A. Characterization of antimicrobial cellulose acetate butyrate/organoclay nanocomposites. *Packag Technol Sci* 2013; DOI: 10.1002/pts.2043.
- 49. Suppakul, P., Miltz, J., Sonneveld, K., Bigger, S. W. Active packaging technologies with an emphasis on antimicrobial packaging and its applications. *J Food Sci* 68:408-420, 2003.
- Rodríguez, F., Sepulveda, H. M., Bruna, J., Guarda, A., Galotto, M. J. Development of cellulose eco-nanocomposites with antimicrobial properties oriented for food packaging. *Packag Technol Sci* 46:149, 2013.
- 51. López, O. V., Giannuzzi, L., Zaritzky, N. E., García, M. A. Potassium sorbate controlled release from corn starch films. *Mat Sci Eng* 33:1583-1591, 2013.
- 52. Türe, H., Gällstedt, M., Hedenqvist, M. S. Antimicrobial compressionmoulded wheat gluten films containing potassium sorbate. *Food Res Int* 45:109-115, 2012.
- Cruz-Romero, M. C., Murphy, T., Morris, M., Cummins, E., Kerrya, J. P. Antimicrobial activity of chitosan, organic acids and nano-sized solubilisates for potential use in smart antimicrobially-active packaging for potential food applications. *Food Control* 34:393-397, 2013.
- 54. Hauser, C., Wunderlicha, J. Antimicrobial packaging films with a sorbic acid based coating. *Procedia Food Sci* 1:197-202, 2011.
- 55. Rivero, S., Giannuzzi, L., García, M. A., Pinotti, A. Controlled delivery of propionic acid from chitosan films for pastry dough conservation. *J Food Eng* 116:524-531, 2013.
- 56. Germinara, G. S., Conte, A., Lecce, L., Di Palma, A., Del Nobile, M. A. Propionic acid in bio-based packaging to prevent Sitophilus granarius (L.) (Coleoptera, Dryophthoridae) infestation in cereal products. *Innov Food Sci Emerg Technol* 11:498-502, 2010.
- Smulders, F. J. M., Paulsen, P., Vali, S., Wanda, S. Effectiveness of a polyamide film releasing lactic acid on the growth of E. coli O157:H7, Enterobacteriaceae and total aerobic count on vacuum-packed beef. *Meat Sci* 95:160-165, 2013.

- Ouattara, B., Simard, R. E., Piette, G., Bégin, A., Holley, R. A. Diffusion of acetic and propionic acids from chitosan-based antimicrobial packaging films. *J Food Sci* 65:768-773, 2000.
- 59. Huang, C. B., Alimova, Y., Myers, T. M., Ebersole, J. M. Short- and mediumchain fatty acids exhibit antimicrobial activity for oral microorganisms. *Arch Oral Biol* 56:650-654, 2011.
- 60. Ruckman, S. A., Rocabayera, X., Borzelleca, J. F., Sandusky, C. B. Toxicological and metabolic investigations of the safety of N-alpha-lauroyl-L-arginine ethyl ester monohydrochloride (LAE). *Food Chem Toxicol* 42:245–259, 2004.
- Rodriguez, E. Cellular effects of monohydrochloride of L-arginine, Nalphalauroyl ethylester (LAE) exposure on Salmonella typhimurium and Staphylococcus aureus. *J Appl Microbiol* 96:903-912, 2004.
- 62. Pezo, D., Navascués, B., Salafranca, J., Nerín, C. Analytical procedure for the determination of ethyl lauroyl arginate (LAE) to assess the kinetics and specific migration from a new antimicrobial active food packaging. *Anal Chimica Acta* 745:92-98, 2012.
- 63. Muriel-Galet, V., Cerisuelo, J. P., López-Carballo, G., Aucejo, S., Gavara, R., Hernández-Muñoz, P. Evaluation of EVOH-coated PP films with oregano essential oil and citral to improve the shelf-life of packaged salad. *Food Control* 30:137-143, 2013.
- 64. Higueras, L., López-Carballo, G., Hernández-Muñoz, P., Gavara, R., Rollini, M. Development of a novel antimicrobial film based on chitosan with LAE (ethyl-N-α-dodecanoyl-L-arginate) and its application to fresh chicken. *Int J Food Microbiol* 165:339-345, 2013.
- 65. Brody, A., Strupinsky, E., Kline, L. *Active Packaging for Food Applications*. *Lancaster*, PA: Technomic Publishing Co., 2001.
- Nies, D. H. Microbial heavy-metal resistance. *Appl Microbiol Biotechnol* 51:730–750, 1999.
- Ibrahim, S. A., Yang, H., Seo, C. W. Antimicrobial activity of lactic acid and copper on growth of Salmonella and Escherichia coli O157:H7 in laboratory medium and carrot juice. *Food Chem* 109:137-143, 2008.
- Ramyadevi, J., Jeyasubramanian, K., Marikani, A., Rajakumar, G., Rahuman, A. A. Synthesis and antimicrobial activity of copper nanoparticles. *Mater Lett* 71:114-116, 2012.
- 69. Bruna, J. E., Penaloza, A., Guarda, A., Rodriguez, F., Galotto, M. J. Development of MtCu + 2/LDPE nanocomposites with antimicrobial activity for potential use in food packaging. *Appl Clay Sci* 58:79-87, 2012.
- Palza, H., Gutierrez, S., Delgado, K., Salazar, O., Fuenzalida, V., Avila, J. I., Figueroa, G., Quijada, R. Toward tailor-made biocide materials based on poly (propylene)/copper nanoparticles. *Macromol Rapid Comm* 31:563, 2010.
- 71. Kamrupi, I. R., Dolui, S. K. Synthesis of copper–polystyrene nanocomposite particles using water in supercritical carbon dioxide medium and its antimicrobial activity. *J Appl Polym Sci* 120:1027-1033, 2011.

- 72. Ozay, O., Akcali, A., Otkun, M. T., Silan, C., Aktas, N., Sahiner, N. P(4-VP) based nanoparticles and composites with dual action as antimicrobial materials. *Colloids Surf B* 79:460-466, 2010.
- 73. Zhang, W., Zhang, Y. H., Ji, J. H., Zhao, J., Yan, Q., Chu, P. K. Antimicrobial properties of copper plasma-modified polyethylene. *Polym* 47:7441, 2006.
- 74. Zhang, W., Ji, J. H., Zhang, Y. H., Yan, Q., Kurmaev, E. Z., Moewes, A., Zhao, J., Chu, P. K. Effects of NH3, O2, and N2 co-implantation on Cu out-diffusion and antimicrobial properties of copper plasma-implanted polyethylene. *Appl Surf Sci* 253:8981-8985, 2007.
- 75. Zhang, W., Zhang, Y. H., Ji, J. H., Yan, Q., Huang, A. P., Chul, P. K. Antimicrobial polyethylene with controlled copper release. *J Biomed Mat Res A* 83:838-844, 2007.
- Wedzicha, R. L. Chemistry of sulphiting agents in foods. *Food Add Contamin* 9:449-459, 1992.
- Opperman, W. J., Fourie, J. F., Sanderson, R. D., Britz, T. J. A monolithic device for in-package SO2 generation for the control of postharvest Botrytis decay of table grapes. *J Food Quality* 22:427-438, 1999.
- Piercey, M. J., Mazzanti, G., Budge, S. M., Delaquis, P. J., Paulson, A. T., Truelstrup Hansen, L. Antimicrobial activity of cyclodextrin entrapped allyl isothiocyanate in a model system and packaged fresh-cut onions. *Food Microbiol* 30;213-218, 2012.
- 79. Ko, J. A., Kim, W. Y., Park, H. J. Effects of microencapsulated Allyl isothiocyanate (AITC) on the extension of the shelf-life of Kimchi. *Int J Food Microbiol* 153:92–98, 2012.
- Castellano, P., González, C., Carduza, F., Vignolo, G. Protective action of Lactobacillus curvatus CRL705 on vacuum-packaged raw beef. Effect on sensory and structural characteristics. *Meat Sci* 85:394-401, 2010.
- Castellano, P., Belfiore, C., Vignolo, G. Combination of bioprotective cultures with EDTA to reduce Escherichia coli O157:H7 in frozen ground-beef patties. *Food Cont* 22:1461-1465, 2011.
- Muthukumarasamy, P., Holley, R. A. Microbiological and sensory quality of dry fermented sausages containing alginate-microencapsulated Lactobacillus reuteri. *Int J Food Microbiol* 111:164–169, 2006.
- 83. Aider, M. Chitosan application for active bio-based films production and potential in the food industry: Review. *LWT-Food Sci Technol* 43:837-842, 2010.
- Silva, J. N., Bezerra, M. C., Farias, P. M. A. Novel and simple route for the synthesis of core-shell chitosan-gold nanocomposites. *Mat Chem Phys* 135:63-67, 2012.
- Fernandez-Saiz, P., Soler, C., Lagaron, J. M., Ocio, M. J. Effects of chitosan films on the growth of Listeria monocytogenes, Staphylococcus aureus and Salmonella spp. in laboratory media and in fish soup. *Int J Food Microbiol* 137:387-294, 2010.

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  - Almenar, E., Catala, R., Hernandez-Muñoz, P., Gavara, R. Optimization of an active package for wild strawberries based on the release of 2-nonanone. *LWT-Food Sci Technol* 42:587-593, 2009.
  - 87. Ahvenainen, R. *Novel Food Packaging Techniques*. Cambridge, England: CRC Press, Woodhead Publishing Limited, 2003.
  - 88. Crank, J. *The Mathematics of Diffusion*. London: Oxford University Press, 1975.
  - Han, J., Floros, J. Simulating diffusion model and determining diffusivity of potassium sorbate through plastics to develop antimicrobial packaging films. *J Food Proc Pres* 22:107-122, 1998.
  - Galotto, M. J., Torres, A., Guarda, A., Moraga, N., Romero, J. Experimental and theoretical study of LDPE versus different concentrations of Irganox 1076 and different thickness. *Food Res Int* 44:566-574, 2011.
  - 91. Cho, Y. W., Han, S. S., Ko, S. W. PVA containing chito-oligosaccharide side chain. *Polymers* 41:2033-2039, 2000.
  - Cohen, J. D., Erkenbrecher, C. W., Haynie, S. L., Kelley, M. J., Kobsa, H., Roe, A. N., Scholla, M. H. Process for preparing antimicrobial polymeric materials using irradiation. U. S. Patent 5428078, 1995.
  - Ozdemir, M., Yurteri, C., Sadikoglu, H. Physical polymer surface modification methods and applications in food packaging polymers. *Crit Rev Food Sci Nut* 39:457-477, 1999.
  - Weng, Y. M., Chen, M. J., Chen, W. Benzoyl chloride modified ionomer films as antimicrobial food packaging materials. *Int J Food Sci Technol* 32:229-234, 1997.
  - 95. La Storia, A., Ferrocino, I., Torrieri, E., Di Monaco, R., Mauriello, G., Villani, F., Ercolini, D. A combination of modified atmosphere and antimicrobial packaging to extend the shelf-life of beefsteaks stored at chill temperature. *Int J Food Microbiol* 158:186-194, 2012.
  - Marcos, B., Aymerich, T., Garriga, M., Arnau, J. Active packaging containing nisin and high pressure processing as post-processing listericidal treatments for convenience fermented sausages. *Food Control* 30:325-330, 2013.
  - Hanusova, K., Štastná, M., Votavová, L., Klaudisová, K., Dobiáš, J., Voldrich, M., Marek, M. Polymer films releasing nisin and/or natamycin from polyvinyldichloride lacquer coating: Nisin and natamycin migration, efficiency in cheese packaging. *J Food Eng* 99:491-496, 2010.
  - Ercolini, D., Ferrocinoa, I., La Storia, A., Mauriello, G., Gigli, S., Masi, P., Villani, F. Development of spoilage microbiota in beef stored in nisin activated packaging. *Food Microbiol* 27:137-143, 2010.
  - Blanco Massani, M., Vignolo, G. M., Eisenberga, P., Morando, P. J. Adsorption of the bacteriocins produced by Lactobacillus curvatus CRL705 on a multilayer-LLDPE film for food-packaging applications. *LWT-Food Sci Technol* 53:128-138, 2013.

- Zemljic, L. F., Tkavca, T., Veselb, A, Sauperl, O. Chitosan coatings onto polyethylene terephthalate for the development of potential active packaging material. *Appl Surf Sci* 265:697-703, 2013.
- Pitak, N., Rakshit, S. K. Physical and antimicrobial properties of banana flour/chitosan biodegradable and self sealing films used for preserving freshcut vegetables. *Food Sci Technol* 44:2310-2315, 2011.
- 102. Manso, S., Cacho-Nerin, F., Becerril, R., Nerín, C. Combined analytical and microbiological tools to study the effect on Aspergillus flavus of cinnamon essential oil contained in food packaging. *Food Control* 30:370-378, 2013.
- 103. Salgado, P. R., López-Caballero, M. E., Gómez-Guillén, M. C., Mauri, A. N., Montero, M. P. Sunflower protein films incorporated with clove essential oil have potential application for the preservation of fish patties. *Food Hydrocolloids* 33:74-84, 2013.
- 104. Ahmad, M., Benjakul, S., Sumpavapol, P., Nirmal, N. P. Quality changes of sea bass slices wrapped with gelatin film incorporated with lemongrass essential oil. *Int J Food Microbiol* 155:171-178, 2012.
- 105. Kanatt, S. R., Rao, M. S., Chawla, S. P., Sharma, A. Active chitosanepolyvinyl alcohol films with natural extracts. *Food Hydrocolloids* 29:290-297, 2012.
- 106. Calatayud, M., Lopez-de-Dicastillo, C., Lopez-Carballo, G., Vélez, D., Hernández Muñoz, P., Gavara, R. Active films based on cocoa extract with antioxidant, antimicrobial and biological applications. *Food Chem* 139:51-58, 2013.
- 107. Siripatrawan, U., Noipha, S. Active film from chitosan incorporating green tea extract for shelf life extension of pork sausages. *Food Hydrocolloids* 27:102-108, 2012.

# **Recycling of Food Packaging Materials**

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#### Abstract

The legislative and technical background for recycling of plastic packaging is discussed in this chapter. Packaging is a short lifetime product, therefore if not managed properly, it can be seen around us as litter. Plastics are excellent packaging materials for their versatility, lightweight and mechanical strength, thus they are used as first choice materials for food packaging. The high quantity of packaging waste has caused legislative measures to be undertaken that have defined the obligations of packaging producers/distributors, recycling and recovery targets, and the waste management hierarchy.

In this chapter the overall structure and components of recovery systems is presented. Recycling options are described with a focus on mechanical recycling. The impact of reprocessing on properties of the main packaging plastics is discussed. Possible problems related to novel packaging materials, in particular their impact on quality of recyclates, are briefly presented.

*Keywords:* Packaging waste, legislation, recovery, recycling, bioplastics, mechanical properties, quality of recyclates

# 11.1 Introduction

Waste management is an important issue for every material. That is clearly visible in the analysis of the lifecycle of petrochemically based products (Figure 11.1). The history of each item starts with a raw material extraction that has to be refined/processed into a material ready for manufacturing a market product in the processing plant. The product, after being used

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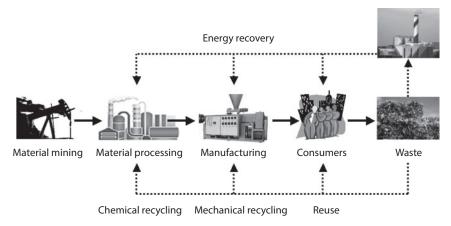


Figure 11.1 Life cycle scheme of petrochemical based products.

by the consumer, eventually becomes waste which is either landfilled or recovered in the form of secondary product or by means of energy recovery from an incinerator. Obviously if a product remains in the landfill it contributes to its expansion and to the environment's pollution. A new portion of raw material must be extracted from Earth in order to meet the requirements of consumers and industry. However, recovery gives a chance of "second life" to waste products, thus both saving the raw material resources and keeping the environment clean and healthy.

Packaging is a product with a very short lifetime, counted frequently in weeks. Sixty percent of all packaging is for food products that helps to save large quantities of food which otherwise would be wasted (in some developing countries even 50%). Current starvation problems of many populations are related not to global food shortages, but rather to unequal food distribution among different world regions. Therefore, besides economic development (availability of money for food), proper logistics, storage and packaging are also important. Packaging should play diverse roles. It should protect a product from damage or contamination, facilitate its distribution, increase shelf life, deliver information allowing identification of the content, expiration date, manufacturer, price, etc.; but it should also attract customers.

According to the World Packaging Organization there are 100,000 packaging manufacturing companies in operation, representing 5 million jobs. After a sharp decline in 2009, global packaging sales recovered in 2010 to \$671 billion, and then the market reached \$700 billion in 2011. Smithers Pira's report, "The Future of Global Packaging," predicts an annual growth of 3% with sales set to exceed \$800 billion by 2016, driven mainly by increasing demand for packaging in the emerging and transitional economies [1]. The U. S. was the largest consumer for packaging in 2010 with a demand of \$137 billion, whereas China was second with \$80 billion, a little ahead of Japan (ca. \$75 billion).

The worth of the European packaging market is estimated at \$127 billion. The amount of packaging being placed on the market in 2010 was 78.7 million tonnes [2]. Considering its short lifetime, every citizen in the 27 Member States generated 156 kg of packaging waste (this quantity varied across European countries between 43 kg in Bulgaria and 202 kg in Luxembourg).

# 11.2 European Policy on Packaging Waste and Raw Materials

Legislation has established a framework for the recycling activity across Europe. European legislation dealing with packaging and the environment should consider a series of European strategies, frameworks and policies.

The first comprehensive legislation on packaging was established in 1994, when the Directive on Packaging and Packaging Waste (Directive 94/62/EC) [3] was adopted by the European Parliament and the Council of Ministers. This Directive aimed to harmonize national measures in order to prevent or reduce the impact of packaging and packaging waste on the environment and to ensure the functioning of the internal market. The Directive requested that Member States introduce systems for the return and/or collection of used packaging and defines specific targets for packaging waste recovery and recycling.

In 2004, the Directive was reviewed to provide criteria clarifying the definition of the term "packaging" and increased the targets for recovery and recycling of packaging waste (Table 11.1). These targets are calculated

	94/62/EC	2004/12/EC
Deadline	30 June 2001	31 December 2008
Overall recovery	50-65%	Min. 60%
Overall recycling	25-45%	Min. 55-80%
Glass recycling	Min. 15%	Min. 60%
Paper recycling	Min. 15%	Min. 60%
Metals recycling	Min. 15%	Min. 50%
Plastics recycling	Min. 15%	Min. 22,5%*
Wood recycling	-	Min. 15%

 Table 11.1 Recovery and recycling targets of packaging waste.

\* exclusively mechanical recycling.

by weight, by dividing the amount of packaging waste recycled by the total amount of packaging waste generated.

As far as the 10 new countries are concerned, Cyprus, the Czech Republic, Estonia, Hungary, Lithuania, Slovakia and Slovenia were expected to meet the 2004 objectives by 2012, Malta by 2013; Poland received an additional two years to comply and Latvia an additional three [4].

Consecutive general Environment Action Programmes (EAP) have guided the development of the EU's environmental policy since the early seventies. Over the past decade (2002–2012), the Sixth EU Environment Action Programme has helped ensure that environmental legislation is in place to tackle most environmental challenges in the EU. In the 6th EAP four priority areas have been identified:

- Climate Change
- Nature and Biodiversity
- Environment and Health
- Natural Resources and Waste

Seven thematic strategies were adopted to constitute the framework for action at EU level in each of the priorities concerned. Within the last priority, the Thematic Strategy on the Prevention and Recycling Waste was developed (adopted 21/12/2005) [5]. The Strategy has been defined as a long-term goal for the EU to become a recycling society that seeks to avoid waste and uses waste as a resource. Therefore, waste prevention, reuse and recycling are promoted, whereas waste disposal should only be considered as the last option (Figure 11.2).

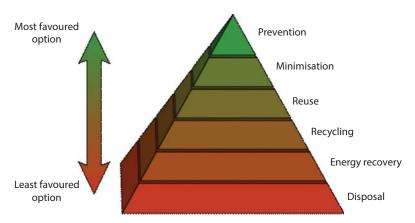


Figure 11.2 Hierarchy of waste management.

The Strategy has identified six key actions to achieve its objectives:

- Life cycle approach;
- Waste prevention policies to be developed by Member States;
- Environmental standards on recycling;
- Simplifying existing legislation;
- Not imposing specific waste recycling or prevention targets; and
- Improving energy recovery from municipal incinerators.

Implementation of these measures has been evaluated in 2011. In the Report on the Thematic Strategy on the Prevention and Recycling of Waste [6] the Commission recommended to:

- Analyse the feasibility of developing eco-design instruments;
- Foster more efficient use of raw materials;
- Ensure the recyclability and durability of products;
- Promote the use of secondary raw materials in products in the context of the Ecodesign Directive [7]; and
- Improve the competitiveness of EU recycling industries by introducing new market-based instruments favoring secondary raw materials.

Another Thematic Strategy formulated within the Natural Resources and Waste Priority was that on the Sustainable Use of Resources. Both strategies are related to the life cycle and resulted in the Raw Materials Initiative (RMI), that was launched in 2008 in order to secure European access to non-energy and non-agricultural raw materials [8,9]. The RMI has focused on the following topics:

- Ensuring access to resources in third countries;
- Fostering a sustainable supply of raw materials from European resources; and
- Boosting resource efficiency and recycling.

In the context of Horizon 2020 it is expected that raw materials will be reflected as a societal challenge. The European strategy for the smart, sustainable and inclusive growth, formally adopted by the European Council on 17 June 2010, shows that in the new integrated industrial policy the Commission has considered waste as an important issue [10].

The experience gathered through the years the recycling market was operating has revealed the role the quality of recyclates plays in market acceptance. This has been emphasized, a.o., in the Lead Market Initiative (2007) [11,12], as a part of the European policy for six important sectors that are supported by actions aimed at lowering barriers in bringing new products or services into the market. It has been stated that innovation is required in the recycling sector in order to enhance the quality of products made of recyclates and reduce the market barriers.

The next legislative measure is the revised Waste Framework Directive 2008/98/EC [13] that has repealed some earlier regulations (the End of Life Vehicles Directive 2000/53/EC and the Directive on Waste of Electric and Electronic Equipment, 2002/96/EC; both also dealing with plastic components) and simplified others in order to provide a set of concepts and targets that should facilitate the recycling business and spread good practices across the EC. They include:

- Promotion of awareness of recycling technologies;
- Promotion of results of research in recycling;
- Supporting eco-innovations in the waste management area;
- Development of recycling standards; and
- Broadening EU market for recyclates.

The Waste Framework Directive has defined *recovery* as any useful use of waste to replace another material. That includes:

- Energy recovery, i.e., using waste as a fuel or other means to generate energy; and
- Recycling, i.e., reprocessing into products or raw materials.

The term *recycling* means:

- Mechanical (material) recycling, i.e., reprocessing by melting, shredding or granulation;
- Chemical (feedstock) recycling, that uses techniques allowing the break down of polymers into their constituent monomers;
- Organic recycling, i.e., composting (aerobic conditions) or biofuel production (without access of oxygen) from biode-gradable plastics.

The REACH Regulation 1907/2006/EC is of some relevance for plastics recycling. It contains specific provisions that facilitate the placing on the market of recycled materials; however some hazardous additives may hinder a compliance with REACH [14]. Some REACH processes are also relevant for improving the resource efficiency of plastics, including recyclability. In particular, restrictions on hazardous additives reduce the risk to the environment associated with using certain plastics.

The Classification, Labelling and Packaging Regulation 1272/2008/EC [15] allows identification of hazardous chemicals and informs consumers of a possible hazard with standard symbols on the packaging labels. Reducing hazardous substances in plastics should also increase their recyclability and reduce risks associated with the use of recyclates.

The European Commission has already formulated the Seventh Environment Action Programme to guide the EU environment policy up to 2020. The 7th EAP is aimed at protecting nature, stimulating sustainable growth, creating new jobs and setting Europe on its way to prosperity and health. A recent study suggested that full implementation of EU waste legislation could save  $\notin$ 72 billion a year, increase the annual turnover of the EU waste management and recycling sector by  $\notin$ 42 billion and create over 400,000 jobs by 2020 [16]. Legal measures should also stimulate investments in the state-of-the-art collection, sorting and recycling infrastructure as well as in innovations which will improve recycling efficiency.

# 11.3 Packaging

# 11.3.1 Packaging Waste

Since the statistical citizen in the 27 Member States generated 156 kg of packaging waste in 2010, the total quantity was 78.6 million tonnes. As a result of the above-described regulations the recycling rate of packaging waste in the EU-27 went up from 54.6% in 2005 to 63.3% in 2010. The rate of overall recovery (including incineration with energy recovery) rose from 66.8% to 76.2%. Figure 11.3 shows the share of different recovery options for the packaging waste in Europe. The major form of recovery in all countries is recycling (only the recycling back to plastics is counted), however, in some countries the energy recovery and the incineration with energy recovery contribute markedly to the overall recovery rate. Member States with landfill rates below 5%, such as Germany, the Netherlands, Denmark, and Belgium, reported above 70% packaging waste recycling [17,18]. As a matter of principle, that option is better than the energy recovery, but even

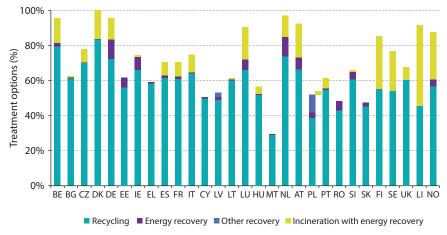


Figure 11.3 Recovery options for packaging waste (Source: Eurostat).

if not all packaging waste may be suitable for recycling, there are no technical reasons why plastics should go to landfill rather than being recycled or incinerated with energy recovery.

Moreover, landfills are not the only places where the packaging waste is being dumped. According to estimations, around 10 million tonnes of litter annually, about 80% of which is plastic, ends up in the world's oceans and seas [19]. It is harmful to the coastal and marine environment, causing problems to sea animals that suffer due to entanglement or ingestion.

# 11.3.2 Plastic Packaging

Plastics are increasingly used not only as packaging, but also in other applications both in the consumer sector and in industrial products. Plastics have been called a 21st century material for their versatility, lightweight, durability, good mechanical properties, low electrical and thermal conductivity, easy processing and recyclability. They are cheap, offer chemical and physical modifications (instead of looking for new monomers to synthesize novel polymers), and are sustainable, e.g., plastics help reduce greenhouse gas emissions and energy consumption [4,20–22].

The world plastics manufacturing capacity (Figure 11.4) has grown annually almost continuously since 1950 (excluding the 2009 crisis), reaching 288 million tonnes in 2012 (y/y growth of 2.8% as compared to 2011) [21]. Asia is the leading plastics producing region (44.6%), with China being the world's number one manufacturer (23.9%).

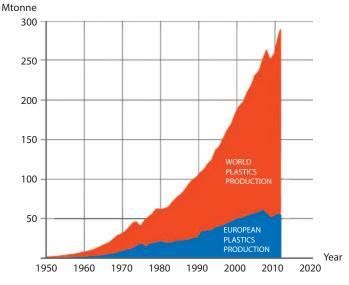


Figure 11.4 Plastics production growth with time.

The plastics industry belongs to the most important European economic pillars, employing over 1.4 million people, showing a turnover of over 300 billion euro (plastics producers, plastics converters, and plastics machinery sector) and generating ca. 26.6 billion euro taxes in 2012. Europe's share of global plastics production (ca. 47 million tonnes) accounts for 20.4%.

The assortment of polymers manufactured in Europe has been presented in Figure 11.5. Major plastics are: polyethylene low density (LDPE) and high density (HDPE), polypropylene (PP), polystyrene (PS) and expanded polystyrene (EPS), polyvinyl chloride (PVC) and polyethylene terephtalate (PET). These polymers contribute up to 73% of the total consumption of plastics in Europe and their recycling will be treated with a special emphasis in this chapter. The group of bioplastics, which has had highly dynamic recent growth, currently constitutes only a small part of total plastic consumption. Their global production capacity is estimated to be 1.2 million tonnes, however the forecasts for 2016 account for 5.8 million tonnes.

Packaging is a leading application sector, representing 39.4% of the total plastics demand, followed by the building, construction and application sector (20.3%). The automotive, electric and electronics, as well as agriculture sectors consume less then 10% each (Figure 11.6).

The total amount of plastics used in the European packaging sector is 18.5 million tonnes, of which polyolefins account for 62%, followed by PET (17.1%), polystyrene (including EPS) and PVC (Fig. 11.7).

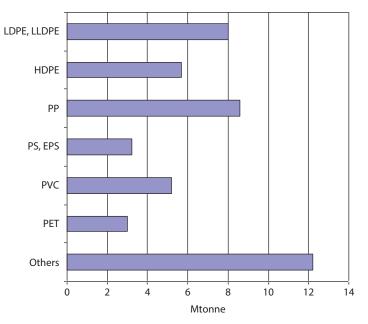


Figure 11.5 Plastics manufactured in Europe.

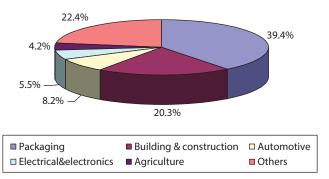


Figure 11.6 Implementation of plastics in different sectors.

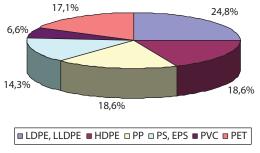
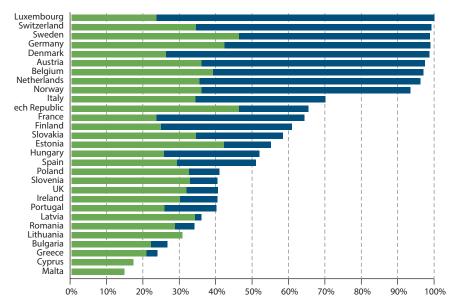


Figure 11.7 Polymers used in the packaging sector.

#### 11.3.3 Plastic Packaging Waste

Because the lifetime of packaging is very short and most plastics are nonbiodegradable, the entire amount of plastics used for manufacturing packaging becomes waste very shortly. That means that 18.5 million tonnes of plastics remain in the environment for a long time, with a possible risk to human health and the environment if it is not recovered [23,24]. Fortunately, as much as 83% of all plastic waste recycled in 2012 in the European Community was packaging. The recycling of plastics is more difficult and costly in comparison to other packaging materials; therefore the amounts of recycled plastic packaging waste vary in different Member States (Figure 11.8).

As the graph reveals, all Member States except Cyprus and Malta achieved recycling rates above the 2008 target of 22.5% (only mechanical recycling was counted). Some countries recover more than 90% of plastic waste, therefore an exchange of best practices on the collection and recovery methods by these countries should allow for improved performance of other Member States [25–27]. One can observe that the best performing countries received such good recovery results due to a high energy recovery rate. These countries have enacted measures leading to a diversion of combustible waste from landfills, equivalent to a landfill ban. The less



**Figure 11.8** Recovery of plastic waste in Europe by recycling (green) and recovery (blue) (Source: PlasticsEurope).

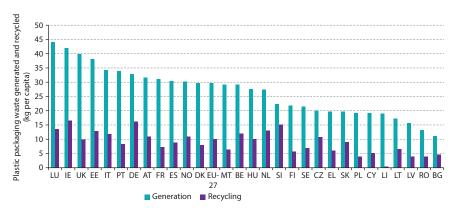
performing Member States apply no such measures and accept waste in landfills with a fee sometimes as low as 7 €/tonne.

The Green Paper on the European Strategy on Plastic Waste in the Environment published in Brussels on 7.3.2013 has announced a review of the waste legislation that will be completed in 2014 [28]. This review will look at the existing targets for waste recovery and landfill.

Sometimes industry is a driver for sustainable development. In 2011 the European plastics industry urged the EU to aim at zero plastics to landfill by 2020. Some regional initiatives towards that goal have already been started. However, as a matter of principle, recyclable materials should not be used as fuel and the energy recovery should be a complement to recycling.

Increasingly scarce resources are focusing interest on the recovery of hardy recyclable plastics, like flexible packaging, especially colorful, fully printed and multilayered films. The environmental impact of plastic carrier bags is considerable. In 2010 there were 95.5 billion plastic carrier bags (1.42 Mt) placed on the EU market, most of them (92%) were for single use. Subsequent to the public consultation on plastic carrier bags held in 2011, the European Commission is considering measures to reduce single-use plastic carrier bags [29]. The recently developed technology is enabling the recycling of materials with binding agents and other additives in a single step into high quality pellets suitable for use in high quality end products.

Figure 11.9 shows the amounts of plastic packaging waste generated and recycled by country in 2010. Luxembourg, Ireland, UK and Estonia have shown plastic packaging waste generated above 38 kg per capita, whereas in Romania and Bulgaria it was only 13 and 11 kg per capita.



**Figure 11.9** Plastic packaging waste generated and recycled in Europe, kg per capita 2010 (Source: Eurostat).

Since plastic waste is categorized as non-hazardous, it can also be imported and exported to non-OECD countries following the procedures of the Waste Shipment Regulation, provided the import is not prohibited by the country of destination. Total exports of plastic waste from EU Member States increased by a factor of five between 1999 and 2011. Most exports went to Asia; however, that means a loss of resources and opportunities for recycling in Europe.

# 11.4 Recovery Systems

The Packaging Directive has obliged the EC Member States to create recovery/recycling systems. Moreover, the Directive introduced two general principles:

- Producer responsibility; and
- "Polluter pays" rule.

Thus, all over Europe different systems were established which have decided how they are going to obey these principles and meet the recovery and recycling targets. Industry (manufacturers, fillers, distributors) is obliged to take back and recycle their sales and transport packaging after use. It is also possible for them to transfer these obligations to other bodies (recovery organizations) that would perform the recovery and recycling of packaging waste in the most economically efficient and ecologically sound manner. Recovery organizations may differ markedly in the logistics solutions and financing details. Some systems are responsible only for household packaging, whereas others also collect the packaging from trade and industry. Recovery organizations operate either in a full-cost or sharedcost system. In the full-cost scheme, the license fee is paid by the companies placing the packed goods on a market and covers the full costs of the collection, sorting, recovery and recycling; whereas in the shared-cost scheme, the fee only includes the expenses spent on a collection or exclusively on the recovery and recycling. Therefore, there are different fee levels in respective organizations [4].

A role of the recovery organizations is coordinating activities of other partners (industry, trade, waste management companies and local authorities) according to contract agreements, which specify mutual obligations, rights and profits (Figure 11.10). It has been learned from the experience gathered through years of operation, that it is very important to build an organization that is transparent and subject to strict internal rules and

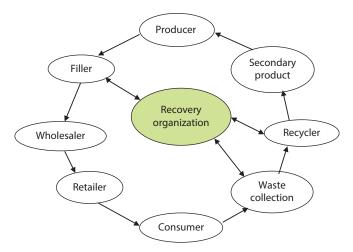


Figure 11.10 Packaging waste management system.

stringent, regular financial audits in order to avoid undesired malpractices and undue costs.

# 11.4.1 Collection

There are three main systems to collect post-consumer packaging waste:

- Bring systems;
- Door-to-door (curbside) collection; and
- Deposits.

The bring system is frequently used in European countries. It is particularly useful and cost effective in towns with many high-rise apartment buildings, and in small communities in rural areas. The bring system uses a number of relatively large containers placed at convenient sites that have good access to the public: adjacent to high-rise buildings, next to shopping centres, etc. A typical arrangement of bring system containers includes one container for waste paper, one or two for glass bottles, one for plastic bottles and cans. Usually the containers differ in colors. The separate collection across Europe is a target of the Waste Framework Directive till 2015. Bring systems can achieve a return rate of 40 percent or more, however the containers can have relatively high contamination rates, depending on the level of the ecological consciousness of a society and how the system has been organized.



Figure 11.11 Containers used for curbside collection.

The curbside collection applies the same principle as a bring system, e.g., the citizens separate the waste at source, but they do it at home. The curbside collection can use containers like the ones used with bring systems, only smaller (Figure 11.11). Recently, it is most common to use plastic bags for the collection of plastic packaging and cans, bags of another color for compost, and a container for residual waste. Glass bottles and paper are often collected at bring systems. The curbside collection can achieve collection rates of 60 percent or more, with a contamination level of around 20 percent.

Deposit systems achieve return rates frequently higher than those of curbside collection; however, they are more expensive.

#### 11.4.2 Sorting

Waste suitable for further material recycling must be of sufficiently high quality so that it is possible to separate the collected waste into material-specific streams. To meet the quality standards of recycled plastics, sorting systems should be installed that are designed to remove contaminants before the recycling process [4,22,30]. Sorting is a substantial cost factor in the budget of recovery organizations; however, the recyclers operating high-capacity plants need a steady source of standardized waste.

*Manual sorting* is the simplest technique, based on the identification by trained inspectors specific plastics in a waste stream being carried on a conveyor. This technique is labor intensive and costly, and may be used efficiently for large items. Manual sorting is facilitated by ID-codes and by a knowledge of typical applications of respective polymers (Table 11.2).

Code	1	2	3	4	5	6
Polymer	PET	HDPE	PVC	LDPE	РР	PS
Application	Drink	Bottles for	Food trays,	Carrier	Margarine	Pots, cups,
	bottles,	milk or	bottles for	bags,	tubs,	fish
	pots,	washing-up	squash or	bin	cups,	trays,
	tubs,	liquids	shampoo	liners	meal	boxes,
	meal				trays,	cuttlery
	trays				bottles	

 Table 11.2 Information supporting manual sorting.

Table 11.3 Density of polymers used for packaging.

Polymer	РР	PE	PS	PA	PET	PVC
Density g/	0.89-0.92	0.91-0.96	1.04-1.08	1.13-1.18	1.30-1.38	1.32-1.45
cm <sup>3</sup>						

*Air classification* allows separating flexible plastics (films) from the whole rigid items using air streams with an adjustable velocity to control the separation process.

*Float-sink* is a method carried out in a tank filled with the fluid of a defined density, thus allowing floating of the less dense materials and sinking of the heavier ones (Table 11.3). The most common fluid is water (making possible a separation of polyolefin from other plastics), but also water-based solutions with NaCl, ZnCl<sub>2</sub> or with methanol. This method is simple but slow, due to a long retention time, moreover it is essential that the size of all flakes is equal.

*Hydrocyclone* is a technique which uses a cylindrical separator with a cone-wall end and applies the principle of centrifugal acceleration, allowing the separation of a water suspension of mixed plastic flakes into the heavy and light fraction based on their specific density. The suspension is pumped tangentially to the hydrocyclone, thus initiating a spinning vortex (Figure 11.12). This technique allows fast and accurate separation.

*Centrifugal sorting* applies the same principle as sorting. The separator is a cylindrical centrifuge ended with cones and equipped with a solid bowl screw with opposite slope of flights. The slurry of shredded plastic waste in a separation liquid is fed axially into the centrifuge and subjected to strong turbulent forces accomplished due to rotation with a very high speed (centrifugal field up to 1600 times higher then gravity). The separation is very fast (residence time in a centrifuge range of 25 s) and achieves efficiency exceeding 99.5%.

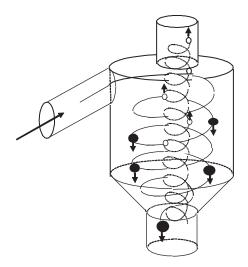


Figure 11.12 Hydrocyclone operation scheme.

*Flotation* is a technique which separates the hydrophobic particles from hydrophilic ones. The aqueous slurry of shredded plastic waste is pumped with air and the bubbles adhere to the hydrophobic particles and carry them out to the surface, forming a froth layer. Hydrophilic particles are wetted by water and stay dispersed in a liquid phase. Some flotation agents may be added to facilitate the separation process, allowing even separation of PET and PVC.

*Electrostatic* sorting uses a triboelectric technique for separation of plastics by their differences in electrostatic charges. The flakes subjected to a frictional contact are charged positively or negatively depending on their dielectric constant, and then are sorted while falling freely between two oppositely charged electrodes that attract the flakes and allow their separate collection according to the triboelectric charge (Figure 11.13). Possible modifications of the sorting set include a rotating drum instead of one plate.

*Melting temperature* is a polymer specific property that allows sorting of mixed polymer waste by differences in the melting point. This method uses a drum/belt heated to temperature of the polymer with the lowest melting point. Such polymer adheres and gets scraped after the drum/belt is turned over, whereas other plastics fall down to a second drum/belt of higher temperature, where another polymer adheres.

Automated sorting applies different techniques of identification for elimination of desired components from the stream of dry mixed waste being transported on a conveyor belt. On their way they are subjected to a light/

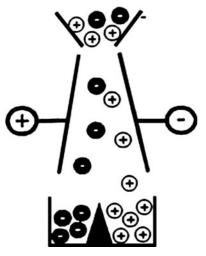


Figure 11.13 Scheme of electrostatic sorting.

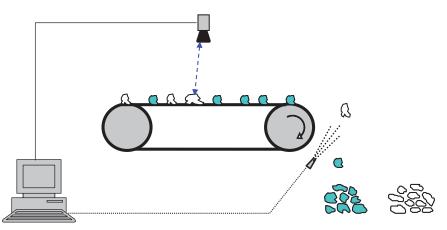


Figure 11.14 Scheme of automatic sorting.

laser beam, and then the detector identifies the single item by comparing a reflected beam to a reference stored in a data base. The item is either ejected by a precisely directed jet of compressed air or is transported further in the main stream (Figure 11.14). The system operates using different sensors (optical, color, spectroscopic – mainly infrared, X-ray) and software, making real-time decisions. For the exact identification of polymers and additives frequently both spectroscopic and optical sensors are integrated in one system. Automated sorting operates with a high throughput (3–5 tph) and high purity (around 95%). Sorting plants frequently use magnet

and/or eddy current units to remove small amounts of steel or aluminium closures.

# 11.4.3 Recycling

The packaging waste, if not reused, should be subjected either to recycling or energy recovery. There are various options to exclude plastic waste from landfills (Figure 11.15).

Figure 11.16 shows how the approach to plastic waste has varied in Europe in recent decades. Initially landfilling was prevalent, but after the Packaging Directive came into force the practice of waste recovery started developing, and since 2005 the amount of waste being landfilled has decreased, even if production of virgin plastics increased. In 2010 the

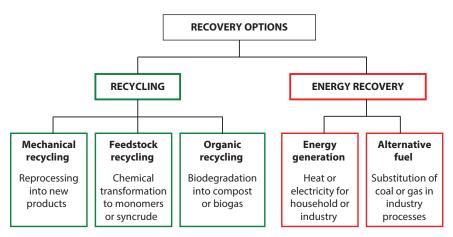


Figure 11.15 Recovery options of plastic waste.

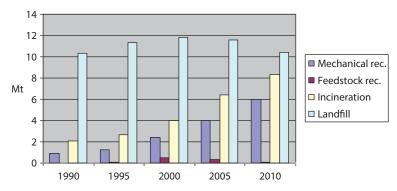


Figure 11.16 Plastic waste management in Europe.

amount of recovered plastic waste was higher than that landfilled and that tendency is increasingly developing. In 2012, of a total of 25.2 Mt plastic waste generated in Europe, recovery accounted for 15.6 MT (61.9%) and landfill for 9.6 Mt (38.1%). From that amount, 6.6 MT (26.3%) plastic waste was recycled and 8.9 Mt (35.6%) incinerated.

Mechanical recycling performed for plastic waste should be well separated by resin, otherwise the products have a limited market, or need upgrading by compatibilization, or by preparing composites. Separation by color is also recommended, since unpigmented recyclate has a greater value due to the larger number of applications. Mixed or contaminated waste plastics should be recovered be means of feedstock recycling or energy recovery.

Feedstock recycling has almost disappeared from European practice for economic reasons, since that option is economically sound only for high waste quantities, which should be available in a continuous manner. Thus, the high cost of transport was the deciding factor in closing major plants.

Organic recycling is limited to a specific group of biodegradable plastics and currently has only a niche market; however its rate of development is very high (20%).

Among all recycling options the mechanical recycling is preferred and solely counted as "recycling" in the annual reports on packaging waste recovery. According to the recent resolution of the European Parliament of 14 January 2014 on the policy regarding plastic waste in the environment, incineration of these wastes should be reduced and landfilling of the plastic waste suitable for reuse or recycling should be entirely banned.

# 11.4.3.1 Mechanical Recycling

The mechanical (material) recycling of plastic waste should be preceded by a range of auxiliary processes that improve the quality of recyclates, making them more attractive to the market.

The technological steps of mechanical recycling include the following operations:

- Sorting;
- Grinding;
- Washing;
- Drying; and
- Melt processing.

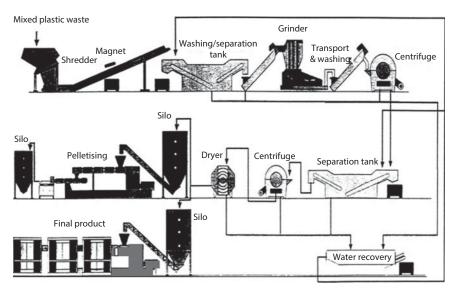


Figure 11.17 Mechanical recycling stages.

A typical set of equipment used for mechanical recycling has been presented in Figure 11.17. Final output form may be flakes/pellets or a final product manufactured directly from the recyclate.

#### Sorting

Sorting of waste is very important due to incompatibility between polymers and their different melting temperatures. Even a small amount of another polymer dispersed in the matrix may markedly change its properties and exclude a whole batch from a desired application.

#### Grinding

The efficiency of some recycling processes depends on a uniformity of the waste size; therefore larger items should be reduced in size with a shredder and then grinded to smaller particles (flakes). In order to avoid the damage of processing equipment and facilitate a smooth separation of different plastics, the metal detector (frequently more than one) has to be located along the way of waste to subsequent technology stages. Size of grinded particles (5–10 mm) is regulated with the sieve mesh.

A variety of technical solutions (whirling and static knives, single, row or cascade location) have been used to provide a desired result, e.g., regular flakes without powder, that should be separated with a cyclone. Waste is normally fed to a shredder/grinder on a conveyor belt or with a feeding

screw, and the flakes are discharged gravimetrically or with a vacuum system.

# Washing

For removing contaminants from packaging waste (paper, glue, labels, detergents, whiteners, remainder of drinks and food, insects, etc.) washing with hot water and detergents or caustic soda should be performed. This prevents defects in the final products, observed as bloomings, bubbles, intrusions and smelts. In addition, recyclates made of an unwashed waste exhibit a deterioration of strength and appearance. Washing should be followed by rinsing with clean water to remove chemicals from a flake surface that could catalyze polymer degradation.

# Drying

Removing water after washing is important to protect polymers like PET and PA from a hydrolytic degradation, or to facilitate a free gravimetric dosing of flakes to the hopper of the processing equipment. This is performed in a centrifuge, followed by a drier with the polymer-specific temperature (Table 11.4).

## Processing

Marketable forms of plastic recyclates are flakes (without further converting), pellets or final products, manufactured from flakes during melt processing. Converting methods are typical for thermoplastics, including extrusion, blow molding, injection molding, press molding, etc. Some changes in the construction of the processing equipment are advisable (Figure 11.18).

These concern the dosing unit (allowing a transfer of flakes to the barrel), the riffled internal wall of a barrel (to push solid flakes forward), the

Polymer	РЕТ	HDPE	PVC	LDPE	РР	PS
Temperature, °C	140	80	75	80	80	80
Time, h	2	1	1	1	1	1

 Table 11.4 Drying parameters for selected polymers.

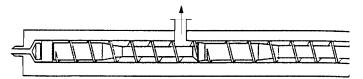


Figure 11.18 Exemplary extruder for waste processing.

deep screw channel in a feeding zone (to take flakes or agglomerates), the venting port at the end of a melting zone (to remove volatiles, water vapor and odors), the filter before the polymer melt leaves a barrel (removing contaminants, gels, solid products of degradation, etc.)

# 11.4.3.2 Impact of Mechanical Recycling on Polymer Properties

Plastic materials most frequently constitute a mixture of polymers with fillers and processing aids. Their properties depend primarily on the structure of polymers—their chemical composition, molecular weight and molecular weight distribution, crystallinity degree, etc. Material characteristics of most interest for end-users, e.g., impact strength, tensile, bending and damping properties, depend on the molecular parameters—similarly also the viscoelastic properties of polymer melts, which are crucial for plastics processing.

The quality of recyclates depends on the entire thermomechanical history of a polymer since it was manufactured. The next step is processing of the polymer into a final product at a high temperature under severe mechanical stresses, depending on the technology and processing parameters. Even if appropriate additives are applied (stabilizers, processing aids) most polymers suffer some degradation. That process leads to a first reduction in length of macromolecules, that also deteriorates the mechanical strength, heat deflection temperature and melt viscosity of polymers. Relatively low structural changes occur during the storage period—especially if temperature is moderate and access to light is limited. The next degradation steps occur during the use period due to the influence of temperature, oxygen, ozone, UV radiation, and humidity. Although some protection is provided by antioxidants and UV stabilizers, they are consumed in the course of exploitation time.

Further degradation takes place during recycling operations (grinding, drying, processing), depending on the applied temperature, stress level and a total residence time in the high shear regions. The final quality of recycled polymers is usually inferior to that of virgin polymers, depending on the polymer type, its initial molecular mass and the extent of degradation. All the above-mentioned degradation reasons constitute some form of energy. If its value exceeds the bonding energy between carbon atoms in polymer macromolecules, chain scission occurs. This is a radical process, which may continue either progressing with a further reduction in the length of macromolecules or may lead to crosslinking/branching reactions.

Different polymers behave differently under possible degradation conditions, depending on their chemical structure, sensitivity to temperature,

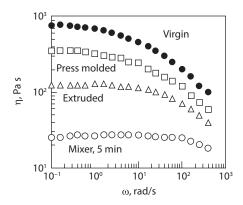


Figure 11.19 Melt viscosity of PP with a different processing history.

humidity, and oxygen access; therefore some are more resistant to mechanical recycling than others [31,32].

The kind of equipment used for recycling also plays a substantial role in the quality of recyclates. For example, single-screw extruders cause more severe degradation than twin-screw machines due to different mechanical stresses and trajectories of melt streams within the extruder barrel, in particular between the static and rotating elements of the machines.

The influence of the processing technology on polymer degradation is presented in Figure 11.19 for a case of virgin polypropylene, subjected to press molding, extrusion or mixing in the internal mixer for 5 minutes at 190°C. The measure of degradation was the melt viscosity  $\eta$ , evaluated with an oscillatory rheometer. All measurements revealed the pseudoplastic character of PP melts; however, they differed in a value of the zero shear viscosity, which is directly related to the molecular weight of a polymer (Mark-Houwink Equation 10.1), and in the length of the Newtonian plateau, which also informs on the extent of degradation. It has been shown that even the press molding caused a drop in the melt viscosity from 750 Pas to 350 Pas, whereas the extrusion brought about a decrease in viscosity down to 120 Pas. Prolonged mixing caused a severe degradation of polypropylene—its melt viscosity fell down to 25 Pas, which evidenced dramatic decrease in the molecular weight of the polymer.

$$\eta_0 = K M_w^{3.4} \tag{11.1}$$

where:

 $\eta_0$  – zero shear viscosity;  $M_w$  – molecular weight; and K – constant. The general dependence of the mechanical performance of a polymer on the molecular weight  $(M_w)$  has been presented schematically in Figure 10.20. Before  $M_w$  falls down below a critical molecular weight  $(M_{wc})$  the material keeps fairly high mechanical properties, however, if the degradation progresses beyond  $M_{wc}$  the mechanical behavior changes dramatically. Since the critical molecular weight of particular polymers is different and sensitivity to degradation as well, in practice one observes that plastic waste exhibits different resistance to multiple reprocessing (recycling).

Mechanical properties can be predicted using Equation 11.2:

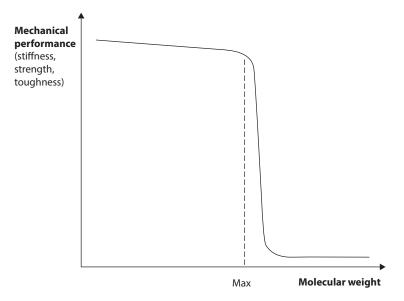
$$P = P_{\omega} - C/M_{w}$$
(11.2)

P – mechanical property (Young's modulus, strength, ultimate elongation);

 $P_{\rm \infty}$  – mechanical property of the polymer with a very high molecular weight; and

C – constant dependent on the kind of polymer and the property selected.

The influence of mechanical recycling on polymer properties has been presented below for selected packaging materials: HDPE, PVC, LDPE, PS, PP and PA6. Since extrusion is commonly used by plastic converters, that technology was chosen for comparison of different polymers. Processability and mechanical strength have been presented as the properties of high



**Figure 11.20** Schematic of the relationship between polymer molecular weight and mechanical properties.

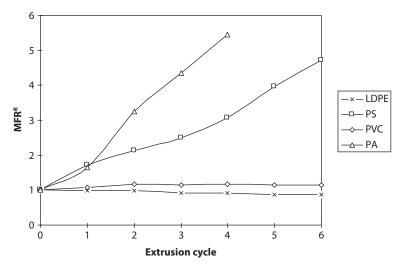


Figure 11.21 Relative melt flow rate as a function of reprocessing steps.

practical value. Processability was estimated by means of the melt flow rate (MFR) and tensile tests were performed in an uniaxial mode. Relative properties have been presented in order to compare the behavior of different polymers on the same graph. The values measured after consecutive extrusions were compared to that of a virgin polymer and marked with an upper index R.

Changes in the relative melt flow rate (MFR<sup> $\mathbb{R}$ </sup>) have been presented in Figure 11.21. High increase in a melt flow rate after consecutive extrusions has been found for polyamide 6. The polymer was so much degraded, that after the 4th cycle a further processing was impossible.

Similar dependence of reprocessing on MFR has been found for polystyrene, but the extent of changes was less expressed than that for polyamide. The LDPE and PVC exhibited high resistance to multiple extrusions. However, contrary to other polymers, MFR of LDPE slightly decreased after reprocessing, which may result in new branchings arising during reprocessing.

Tensile properties are also related to the chemical and physical state of polymers. Young's modulus and the elongation at break are known to be sensitive indicators of the structural parameters. The elongation at break of PA6 only slightly decreased after initial extrusion courses (Figure 11.22). A tremendous decrease, reaching 80%, was observed after the third extrusion cycle, thus confirming a conclusion on the extended polymer degradation.

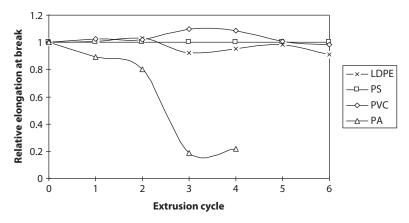


Figure 11.22 Relative elongation at break as a function of extrusion cycles.

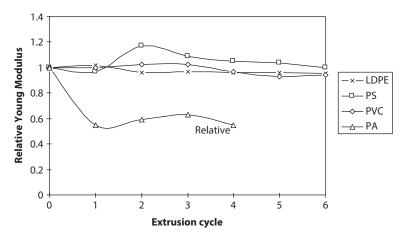


Figure 11.23 Relative Young's modulus as a function of reprocessing steps.

There were no changes observed in relative elongation values for LDPE, PVC and PS.

The tensile modulus of PA6 exhibited a substantial decrease just after the first extrusion, which accounted for 50%—consecutive extrusions did not cause a further change in the stiffness of the polymer (Figure 11.23). This finding has confirmed an advanced degradation of polyamide, which was evidenced by MFR results. Young's modulus of other polymers did not change its value in comparison to the virgin ones. This has confirmed the conclusion that LDPE, PVC and PS can be recycled without objections.

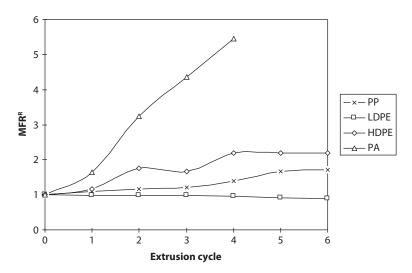


Figure 11.24 Relative melt flow rate as a function of reprocessing steps.

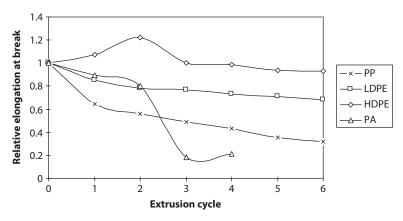


Figure 11.25 Relative elongation at break as a function of extrusion cycle.

A comparison of the sensitivity to degradation during consecutive extrusions of PA6 with polyolefins has been presented in Figures 11.24 and 11.25. Polyamide degraded with a very high rate, however, some increase in flowability was also observed for PP and HDPE, thus indicating the chain scission reactions. The LDPE exhibited only a slight decrease of MFR, which was interpreted in terms of an increased branching density.

Tensile properties revealed not only a dramatic degradation of PA6, but also a steadily progressing chain scission in polypropylene, that was observed as an increase in Young's modulus and a decrease in the elongation at break (Figure 11.25). Some decrease in the ultimate elongation of LDPE was interpreted as a result of branching and crosslinking reactions developing stepwise in the polymer.

The highest stability in the mechanical recycling exhibited HDPE, however, LDPE and PVC can also be recommended for multiple reprocessing, although a restabilization of poly (vinyl chloride) should be considered due to a high temperature sensitivity of that polymer.

#### 11.4.3.2.1 Recycling of PET

A major PET waste in a recycling stream is bottles, which can be converted to fibers (for clothing, e.g., t-shirts, fleeces, jeans, or geotextiles), foils, bottles (even for food applications with B2B technology), strapping tapes or technical details. European collection of PET bottles attained 1.68 Mt (more than 60 billion bottles); that is over 52% of all bottles available.

The mechanical recycling of PET is a predominant recovery technology; however, it is hampered by numerous constraints. Among the most important are those related to the hydrolysis leading to the depolymerization of poly (ethylene terephtalate). Contaminants that generate acidic compounds (PVC labels, seals or sleeves, rosin acid from glue, EVA cap liners) or caustic soda (remaining from washing) cause that problem during extrusion. The same happens if PET waste is not dry enough—initial humidity of flakes is 0.7%, however before extrusion it should not exceed 50 ppm, otherwise a reaction reverse to polycondensation occurs [33].

The influence of degradation caused by processing on molecular parameters has been presented in Figure 11.26. The intrinsic viscosity IV (related to a molecular weight) of virgin PET is markedly higher than that after processing into a bottle (injection molding followed by blow molding). The recyclate derived from a waste bottle suffered a further IV decrease, making it not useful for manufacturing bottles (required IV is above 0.75).

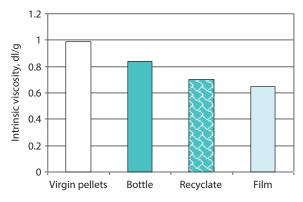


Figure 11.26 Intrinsic viscosity of PET with different processing history.

Waste PET from X-ray film exhibited the lowest molecular weight (intrinsic viscosity 0.65 dl/g).

The problems related with PET depolymerization can be solved with solid-state polycondensation, which should be performed with a hot inert gas (nitrogen) or in a vacuum chamber at temperature of 200°C. The process takes 4–6 hours and by advancing the polymerization degree it provides a material of increased intrinsic viscosity and contaminant-free. Such recyclate is of the food grade and exhibits high mechanical strength.

Even if PVC at a level above 50 ppm is a principal problem, other difficulties may be caused by novel multilayer bottles with enhanced barrier properties. Frequently that barrier is EVOH, in which content during recycling above 500 ppm should be avoided because of the danger of acidic hydrolytic degradation. Another barrier material is PEN, which if recycled with PET causes the secondary material to become brownish and fluorescent. Currently there are no restrictions on clear plasma coatings, provided the carbon level in not high.

Closures and labels on PET packaging should be of polypropylene or polyethylene, as these polymers are easy to separate as low-density materials. Some problems are caused by sleeve labels covering more than 40% of the bottle surface. Without sufficient clear area available, such bottles cannot be identified with sensors and are rejected by the automatic sorting equipment.

Some specifications of PET mechanical recycling require additional operations preceding extrusion, e.g., crystallization, that should be performed at 120°C for 30–60 min., and drying at 150°C for 4 h. Crystallization prevents the sticking together of PET flakes during drying, up to forming aggregates, that would happen if the polymer was in an amorphous phase, which is a normal PET state in bottles, films and sheets. The difference in the thermomechanical behavior of poly (ethylene terephtalate) at both physical states has been presented in Figure 11.27. The range of temperature transitions in the crystalline PET is higher for 14.5°C in comparison to that in the amorphous polymer.

In recent years one can observe in the market an increasing amount of bottles made of poly(lactic acid) (PLA) that are collected in the same stream as PET bottles. Recycling of PLA together with PET should be avoided for the reason that PLA melts at the temperature of PET drier, thus complicating the recycling process. In addition it causes a deterioration of PET mechanical properties and a loss in transparency, as these polymers are incompatible.

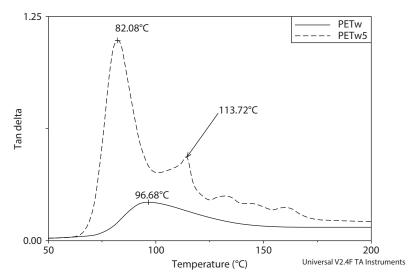


Figure 11.27 Thermomechanical properties of PET amorphous (w5) and crystalline (w).

#### 11.4.3.2.2 Recycling of Polyethylene

The wastes of interest are HDPE bottles for milk or other liquids, as well as different containers, tubes and films. Efficient separation with conventional density separators is easy, provided that the fillers (talc, calcium carbonate) were used in such an amount that polyethylene flakes do not sink in water.

The principal contaminants of HDPE waste are made up of polypropylene bottles and closures. The PE and PP cannot be easily separated with water (density of both is below 1 g/cm<sup>3</sup>), therefore polypropylene may form inclusions in the HDPE matrix if both polymers are processed together. This is due to the higher melting temperature of PP (ca. 165°C) than HDPE (ca. 130°C).

Another problem is caused by HDPE containers used for motor oil that not only leaves a specific odor in recyclates, but also migrates into the flakes, thus plasticizing the polymer and changing its mechanical and thermal properties. In contrast to the odor derived from milk bottles, its odor cannot be extracted during a hot washing stage.

The next factor decreasing the market value of recyclates is mixing waste bottles with tubs and dishes, since HDPE grades used for their manufacturing are different. Bottles are produced by blow molding technology, which does not require such a high melt flow index as the injection-molded goods need.

As a result of recycling, the melt flow rate of polyethylene slightly decreases due to branching and crosslinking. Chain scission occurs only if the processing temperature is high (above 240°C).

Specific problems have arisen in recent years after oxo-degradable materials entered the market. These plastics are made mainly of polyethylene with additives (usually metal salts), that accelerate their degradation when exposed to light and/or heat. Packaging made of oxo-degradable plastics is frequently claimed to be biodegradable or oxo-biodegradable. As a matter of fact, the bioassimilation of microorganisms is possible only for the moderate- or short-length molecules. The extent of polyethylene macromolecules degradation caused by pro-degradants depends on weathering conditions and the timescale (usually years), thus when a true biodegradation starts is not known [34]. Such waste cannot be mixed with compostable packaging, since it does not degrade within the composting period. Mechanical recycling also should be excluded due to the additives, which accelerate degradation causing a deterioration of the mechanical performance. Oxo-degradable waste in landfills behaves like regular polyethylene because normally there is no oxygen access to the landfill interior. The recovery route of choice for oxo-degradable packaging waste should be incineration with energy recovery.

## 11.4.3.2.3 Recycling of PVC

Usually PVC bottles are recycled. The polymer is easily separated in polyolefins, however PVC is of very similar density to PET, therefore these components are difficult to separate in the conventional density separators. Even small amounts of PET cause quality problems due to a higher processing temperature of PET (250–260°C) than PVC (180–190°C). Thus, unmelted PET can lead to a rapid obstruction of filters in the extruder or it will form spots dispersed in a clear PVC matrix.

The main disadvantage of PVC is a limited thermal stability that requires the addition of heat stabilizers to prevent an extended degradation. Because the stabilizer is consumed during processing of a primary product, the thermal stability of recycled PVC is remarkably reduced and for further processing cycles a restabilization should be considered.

## 11.4.3.2.4 Recycling of PP

The major contaminant of polypropylene waste is HDPE from bottles and closures. Both polymers have a density < 1 g/cm<sup>3</sup> and float on water, thus are difficult to separate. Because polyethylene melts before PP, small amounts of HDPE (up to 5%) should be acceptable. Higher polyethylene levels are not recommended due to incompatibility.

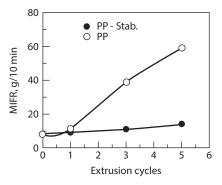


Figure 11.28 Influence of stabilization on melt flow rate of polypropylene.

The use of PVC labels and sleeves should be avoided since thin foils are not separated gravimetrically and carried over with a floating fraction that can cause discoloration and malodor.

Manufacturing of technically advanced products from PP recyclates needs an additional amount of antioxidants and stabilizers. The influence of stabilization on the melt flow rate of polypropylene as a function of reprocessing cycles has been presented in Figure 11.28. The PP with addition of stabilizers (antioxidant Irganox 1010 and stabilizer Irgafox 168) keeps MFR value without remarkable changes, whereas the non-stabilized recyclate exhibited an increase of MFR with consecutive recycling steps, thus evidencing the chain scission typical for polypropylene degradation. Moreover, shorter polymer chains may arrange easier into a crystalline order, thus the degraded polypropylene becomes increasingly brittle.

## 11.4.3.2.5 Recycling of PS

A colorless polystyrene waste has the highest recycling value. Recovery of transparent polystyrene packaging has no specific restrictions, besides labeling with PET or PVC, as all these components sink in water and are difficult for sorting with the most popular density separators. However, aluminium lids are acceptable, especially the peel-off ones.

## 11.4.3.3 Chemical Recycling

Mixed plastics, multilayer packaging and contaminated waste used to be rejected by the collection stream as not being suitable for mechanical recycling. Although some fractions may be used for manufacturing furniture, insulations, pallets and fencings (by intrusion of heavily contaminated polyolefins), the rest should be subjected to a chemical recycling or incinerated.

*Feedstock recycling*, as a technique aimed at the degradation of polymer macromolecules to monomers or to simple hydrocarbons, requires the infrastructure typical for chemical plants and also similar parameters (high temperature and pressure). The polymers manufactured from chemicals derived from feedstock recycling are of high quality, therefore they are market acceptable and food contact permitted.

Mixed plastic waste loaded together with coal in a high temperature reactor ( $1100-1300^{\circ}$ C) decompose to the synthesis gas (CO, H<sub>2</sub>), a principal substrate for the chemical industry. It is used for production of methanol, synthetic fuels, acetic and formic acid, as well for ammonia synthesis.

The next technique is converting mixed waste plastics into *hydrocarbon fuel*, which is increasingly important as crude oil price is rising. Another benefit is a reduced foreign oil dependency, the security of energy and environment protection. Shredded plastic wastes are fed to the reactor at a temperature above 400°C, where plastics are subjected to cracking and vaporization. After condensing, the liquid oil-like products are collected. Their composition depends on the reactor temperature—the lower the temperature the more oil and less coke is manufactured, the higher the temperature the more gases, more coke and higher reaction rate. While performing cracking with an access of hydrogen one receives products of higher quality, without unsaturated hydrocarbons.

The controlled degradation at high temperature can be performed for any kind of plastics (polyolefin is preferred), however, PVC should be rejected since due to its dehydrochlorination the intensive emission of hydrochloric acid occurs, thus causing a corrosion of metal parts. Another reason is emission of a deadly poison named dioxins that accumulate in living tissues.

The reduction of iron ore is a specific recovery method of waste plastics. Steel is produced from hot metal, which still contains up to 4% carbon (C). This percentage needs to be reduced to a maximum of 2% down to zero, depending on the steel grade. The reduction of ore (iron oxide) into a metal is normally done with coke, loaded to the blast furnace together with the ore. Part of the coke can be substituted with waste plastics, preferably polyolefins, as hydrocarbons enter into the reaction with oxygen, linking it into carbon dioxide and water.

The waste plastics are agglomerated or pelletized and injected with a compressed air through the long pipe systems into the blast furnace. Around half a million tonnes of waste packaging is recovered with this method in Austria and Germany, saving a lot of space in landfills, tens millions GJ of energy and around 1 million tones of carbon dioxide, sulphur dioxide and a lot of dust.

Several chemical transformations are possible with poly (ethylene terephtalate), as all polyesters have functional end groups ready to react with other chemicals.

*Glycolysis* of PET waste is a reaction performed with excess ethylene glycol under pressure at a temperature of 200°C, giving bis-(hydroxyethyl) terephtalate as a product. That compound is used as a monomer for PET synthesis.

*Methanolysis* can be performed under similar conditions, but with methanol instead of ethylene glycol. The products are dimethylterephtalate and ethylene glycol, both being substrates for PET production.

*Hydrolysis* can be performed with water in an acidic or alkali (caustic soda) environment. The products are terephtalic acid and ethylene glycol, again useful for PET manufacturing. However, this method is less established than glycolysis and methanolysis.

*Saponification* is an alkali treatment of PET waste in a multistep process. The products are ethylene glycol and disodium terephtalate, or ethylene glycol, terephtalic acid and sodium sulphate, e.g., the raw materials for PET production.

## 11.4.3.4 Organic Recycling

Organic recycling is related to biodegradation, e.g., the enzymatic activity of bacteria, microorganisms, fungi and insects, that transforms biodegradable plastics into compost (with oxygen access) or biogas (at anaerobic conditions). Organic recycling brings about not only a reduction of the packaging waste amount in landfills and emission of greenhouse gases, but also helps in reaching the limits of the landfilled biodegradable municipal waste according to Directive 1999/31/EC (current limit is max. 50%, 2016 limit accounts for max. 35% of the amount landfilled in 1995).

Composting enables an increase in the amount of organic carbon in soil and a decrease in the consumption of fertilizers by 30-50%. The process requires specific conditions: oxygen access, controlled temperature  $(20-37^{\circ}C \text{ at a first stage, then } 50-65^{\circ}C)$  and humidity (40-45%) to provide high quality compost. The product of composting is humus (rich in mineral salts), carbon dioxide and water. The composting and quality control parameters have been defined in Standard EN13432 together with acceptable limits of selected hazardous substances and a disintegration level. Moreover, the compost should exhibit no negative impact on plants. Compostable packaging should be labeled with appropriate symbols (Figure 11.29).

Germany	Belgium	Finland	USA	Japan
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EN 13432 ASTMD6400	EN 13432	EN 13432	ASTM D6400	GreenPla

Figure 11.29 International labeling of compostable packaging.

The industrial composting of plants also sets a time scale for the process, therefore not every biodegradable material is compostable. The total time should not exceed 12 weeks. The process stages are as follows:

- Separation (glass, plastics, metals, batteries, etc.);
- Grinding;
- Sieving;
- Composting (prism forming, agitation every 1–2 weeks, water supply);
- Maturing; and
- Sieving (fractions 10 mm and 25 mm).

Biogas generation is a process of waste biodegradation without oxygen access which produces a gas containing methane (50–80%), carbon dioxide (20–40%), water vapor, nitrogen and oxygen. An amount of 100 m<sup>3</sup> of biogas allows the generation of 400 kWh of electricity. The cost of a multifunctional biogas plant capacity of 30–50,000 t/a is approximately 20 million  $\in$ .

## 11.5 Bioplastics

Biomass is considered as an option that may help in reducing the dependence on imported oil and gas and improving the environmental balance due to reduced carbon dioxide emissions. Looking for free access to raw materials, industry is moving nearer to nature, therefore polymer materials which are produced from renewable resources (biobased) are the focus of growing interest [35,36]. A similar trend is observed for a group of biodegradable polymers, e.g., materials that undergo degradation caused by microorganisms and meet specific international standards (EN 13432, ISO 17088). Both terms are frequently used synonymously, which is wrong, since biodegradables are both poly(lactic acid) (PLA) and starch (biobased), as well as polycaprolactone and aliphatic-aromatic polyesters (fossil derived). On the other hand, bio-polyethylene and bio-polypropylene are biobased, but do not degrade when exposed to microorganisms. Nevertheless, both biobased and biodegradable are called bioplastics.

Bioplastics play an increasing role in packaging applications (both rigid and flexible), as their development has been encouraged in Europe in a different manner (lower packaging tax tariff or even derogation from the recovery fee). Therefore one should expect an increased quantity of packaging made of bioplastics entering the recycling scheme.

### 11.5.1 Biodegradable Polymers

Biodegradable polymers frequently exhibit properties comparable to commodity plastics but their applications are intended mainly for single-use food packaging, containers, cups, plates and cutlery because of their sensitivity to undergo the microbially induced degradation. Thus, the preferable recycling technique for biodegradable polymers should be composting (organic recycling). However, during processing some amounts of waste remain, which could be mechanically recycled similarly to a majority of commodity plastics at the processing site. Moreover, some amounts of biodegradable packaging waste can be mixed with other plastic waste, as there are not yet individual bioplastic collection systems. Once their critical volumes in the overall waste stream are achieved, one should expect that the bioplastics stream will be separated for suitable recovery methods, depending on local infrastructures. Besides composting, mechanical recycling could be considered, especially when sufficient volumes of homogeneous waste are available, since some biodegradable plastics are capable of being multiply reprocessed (Figures 11.30 and 11.31).

The PLA exhibited only slight changes in the tensile modulus after consecutive extrusions within the 10-times extrusion program (Figure 11.30). The value 2,200 MPa measured for a virgin polymer was different in some recycling stages for only 10%. This is a confirmation that such a processing history still keeps the material in a high value range for mechanical properties (Figure 11.20). The same statement is valid for the tensile strength of recycled PLA (Figure 11.31).

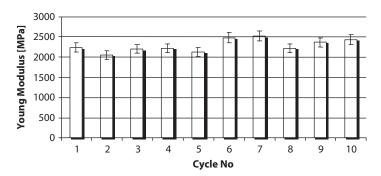


Figure 11.30 Young's modulus of PLA as a function of extrusion cycles.

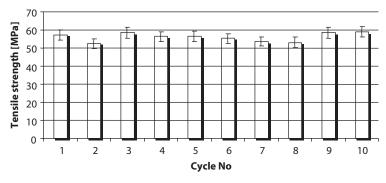


Figure 11.31 Influence of recycling on tensile strength of PLA.

Poly(lactic acid) is a biodegradable material produced from natural, renewable raw materials. It is characterized as a high gloss and transparent material, with high barrier properties for gases, good mechanical properties, and good processability. It is used in many industrial sectors, mainly in the packaging industry (for bottles, beakers, food trays, cups, plates and cutlery), where PLA has to compete with cheap synthetic plastics, and in medicine. It is a crystalline thermoplastic polymer with a relatively high melting point (150–180°C) and with a glass transition point 54–56°C.

The principal PLA manufacturer is NatureWorks, a company that offers several grades under the brand name Ingeo. Due to its relatively high price, it is beneficial to recycle PLA.

Another biodegradable polymer is starch, which occurs in nature as discrete granules. Starch is a polysaccharide mixed of two components: the linear amylose and the highly branched amylopectin. In a native state it is brittle and not processable, because its melting temperature is higher than the degradation temperature. However after addition of plasticizers one receives thermoplastic polymers with moderate mechanical strength, flexibility, and barrier properties for commercial packaging and consumer products. Depending on the plasticizer amount the properties of thermoplastic starch can vary greatly (Tg varies between  $-50^{\circ}$ C and  $110^{\circ}$ ).

Novamont is a leading company in producing various types of starchbased blends with other polymers for film applications (bags, overwraps, mulch films), sanitary products, etc.

## 11.5.2 Biobased Polymers

The principal polymer used in the packaging industry is polyethylene, manufactured by polymerization of ethylene. Traditionally, this monomer is produced from crude oil by the steam cracking of naphta or by ethanol dehydration.

The first trials for producing PE from bioethanol were performed in the 1980s by Braskem. Unfortunately, low oil prices and problems with the biotechnology processes caused the technology to be unsuccessful at that time.

Currently, a revival of that concept has been observed. Bio-PE is produced at industrial scale from bioethanol derived from sugarcane. Some other renewable feedstocks can also be used, including sugar beet, maize, wood, wheat, corn, and other plant waste.

Bio-PE has the same chemical, physical, and mechanical properties as petrochemical polyethylene and has been used for manufacturing plastic bags, milk and water bottles, food packaging films, etc. Braskem is the largest producer of bio-PE, also having bio-PP and bio-PVC in the company portfolio.

Because of the structural identity of biobased polymers with the fossilbased equivalents, packaging made of both grades can be recycled with the same methods and in the same waste stream without any need of their separation. The mechanical recycling of biobased polymers together with traditional polymers has no effect on the quality of recyclates.

## 11.6 Polymer Nanocomposites

Nanocomposites constitute two-phase materials with nanoparticles of a different size and shape dispersed in the polymer matrix. Nanocomposites filled with nanosize platelets are becoming popular as high barrier packaging materials due to a specific dispersion state of the filler that causes a much slower torturous penetration of gas particles through the composite.

Moreover, the nanofillers are incorporated in very low quantities (1–5 wt%), allowing reduction of filler consumption and making the products lightweight. Nevertheless, the change in properties of a matrix is comparable to that achieved with ten times higher loadings of traditional fillers. In addition, the tiny size of the filler (lower than a length of a light wave) makes the composite transparent, which is unique for composites and favorable for packaging.

Mechanical recycling of polymers with such low filler loadings does not negatively influence the material quality [37]. Properties of recycled nanocomposites depend on the kind of equipment used for recycling, the reprocessing number and the extent of the polymer matrix degradation. Recycling of nanocomposites sometimes brings about an improvement in selected properties. The results presented in Figure 11.32 show a decrease in the oxygen permeability of PLA filled with 5 wt% of organically modified montmorillonite (MMT) after the fifth extrusion. The results may be interpreted in terms of an improved intercalation of MMT nanofiller in PLA matrix.

However, a better dispersion of MMT clay platelets in the polymer does not necessarily improve mechanical properties. The relative tensile strength as a function of extrusion cycles has been presented for PLA and PLA/ MMT nanocomposite in Figure 11.33. The values measured after recycling using a twin-screw extruder were compared to that of a pristine PLA and the nanocomposite prepared from a masterbatch. Any influence of recycling on the material performance was not found, only a slight increase in the tensile strength was observed after ten extrusion cycles. Since the

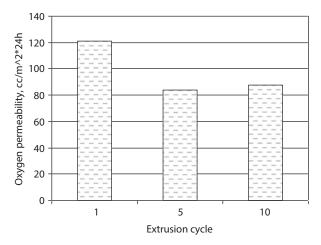


Figure 11.32 Oxygen permeability of recycled PLA/MMT nanocomposite.

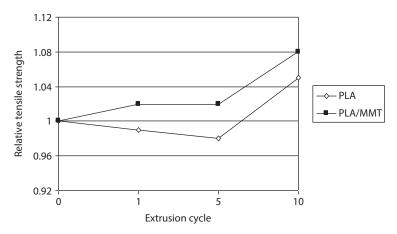


Figure 11.33 Relative tensile strength of recycled PLA and PLA/MMT nanocomposite.

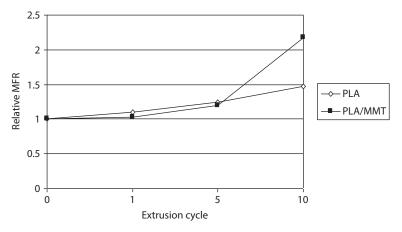


Figure 11.34 Relative melt flow rate of recycled PLA and PLA/MMT nanocomposite.

character of changes is identical for both PLA and PLA/MMT composite one can suppose that the reason is the polymer degradation rather than the quality of nanofiller dispersion.

Relative processability of PLA and PLA/MMT nanocomposites as a function of extrusion cycles has been presented in Figure 11.34 by means of the relative melt flow rate. One can observe the effect of polymer degradation, which is illustrated by a systematic increase of MFR after consecutive extrusions, up 50% after ten cycles. However, PLA/MMT nanocomposite exhibited a strong increase in the melt flow rate at that stage that should be

attributed not only to the polymer degradation, but rather to a significant change in the mode of nanofiller dispersion (e.g., intercalation).

The nanofillers can be applied to up-grade waste polymers, however that should be done with care, since the frequently used clays are modified predominantly with quaternary ammonia, which are unstable at high temperature. Decomposition of these compounds above 200°C generates byproducts that cause an acidic degradation of the polymers manufactured by polycondensation, like poly (ethylene terephtalate). Nevertheless, selection of proper modifiers may result in an improvement of PET stiffness and flexibility with layered silicates.

## 11.7 Polymer Blends

The mechanical recycling of waste plastics contaminated with other polymers or the reprocessing of multilayer packaging gives a product in the form of heterogeneous materials, with properties that depend on the composition of such blends, a compatibility of components, the viscosity and elasticity ratio of molten polymers, and on interfacial adhesion and other parameters that influence the morphology generated in the course of processing. The phase structure of heterogeneous materials may change during recycling, thus causing significant changes in their properties. The influence of recycling on morphology of polymer blends has been presented for two exemplary systems: LDPE mixed with PS and PP mixed with PA6.

Observations of the cold-fractures samples with a scanning electron microscope revealed that the morphology of LDPE/PS (2/1 weight ratio) is of the interpenetrating type (Figure 11.35a). Comparison of the initial morphology with that after five extrusions has revealed its change into the disperse-type morphology (Figure 11.35b). Both materials exhibited different mechanical properties, since in the first case both components equally participate in resulted properties, whereas in the second the characteristics of the matrix polymer and the interfacial adhesion become dominant; moreover the dispersed phase may play a specific role. The total level of the thermomechanical stress imposed on the polymers may also cause the macromolecular defects, which initiate radical processes and change the interfacial interactions. This has been confirmed by Figure 11.35b, where domains of the dispersed phase were smaller and more uniform in size, which suggested a compatibilization of components in the system.

Similar conclusions can be drawn from observations of the initial morphology and that after ten extrusions of PP/PA 80/20 blend (Figure 11.36). The blend exhibited the dispersed type of morphology; however, the initial

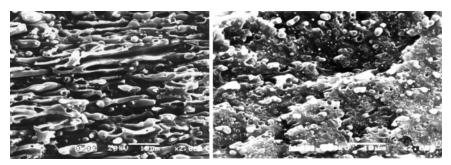


Figure 11.35 LDPE/PS 2/1 initial morphology (left) and after five extrusion cycles (right).

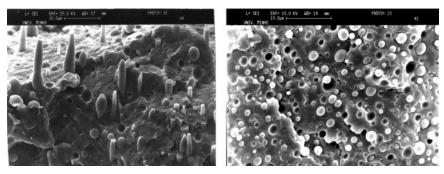


Figure 11.36 PP/PA 80/20 initial morphology (left) and after ten extrusion cycles (right).

one was fiber-like, whereas after recycling it had changed into a dropletlike one. Material changes in a microscale were transposed into macroscopic properties.

## Acknowledgements

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## References

- 1. The Future of Global Packaging to 2018, Smithers Pira Market Intelligence, 2013
- 2. http://www.europen-packaging.eu/

- 3. European Parliament and Council Directive 94/62/EC on Packaging and Packaging Waste, EUR Lex 31994L0062, 1994.
- 4. Kozlowski, M., ed., *Plastics Recycling in Europe*, Ofic. Wyd. Pol. Wr., Wroclaw, 2006.
- 5. *Thematic strategy on the prevention and recycling waste*, Report from the Commission to the European Parliament, 2005.
- 6. On the thematic strategy on the prevention and recycling of waste. European Commission Report, 2011.
- Directive 2009/125/EC of the European Parliament and of the Council establishing a framework for the setting of ecodesign requirements for energyrelated products, EUR – Lex, 2009.
- 8. *The raw materials initiative meeting our critical needs for growth and jobs in Europe*. European Communication, 2008.
- 9. On the implementation of the Raw Materials Initiative. European Commission Communication, 2013.
- 10. *Europe 2020. A strategy for smart, sustainable and inclusive growth, European Commission Communication,* Brussells, 2010.
- 11. *A lead market initiative for Europe*, European Commission Communication, 2007.
- 12. Final Evaluation of the Lead Market Initiative, Centre for Strategy and Evaluation Services Oxford Research, Sevenoaks, July 2011.
- 13. Directive 2008/98/EC of the European Parliament and of the Council on waste and repealing certain Directives, EUR Lex 32008L0098, 2008.
- 14. Regulation 1907/2006/EC of the European Parliament and of the Council on the Registration, Evaluation, Authorisation and restriction of Chemicals (REACH), 2006.
- 15. Regulation 1272/2008 of the European Parliament and of the Council on the Classification, Labelling and Packaging of Substances and Mixtures, 2008.
- 16. A stronger European industry for growth and economic recovery industrial policy communication update, European Commission Communication, 2012.
- 17. Source of statistical data: Eurostat, PlaticsEurope, EuPR, EuPC.
- 18. *Being wise with waste: the EU's approach to waste management*, Luxembourgh Office of the European Union, 2010.
- 19. *Marine litter: A global challenge*, United Nations Environment Programme, http://www.unep.org/pdf/unep\_marine\_littera\_global\_challenge.pdf, 2009.
- 20. *The contribution of plastics products to resource efficiency*, GUA Consulting, Vienna, 2005.
- 21. Plastics the Facts, Plastics Europe, 2013.
- 22. La Mantia, F. P., ed., Handbook of Plastics Recyling, Rapra Technology, 2002.
- 23. *Plastic waste in the environment*. Revised final report for European Commission DG ENV, Bio Intelligence Service, Paris, 2011.
- 24. Brandt, B., and Pilz, H. *The impact of plastic packaging on life cycle, energy consumption and greenhouse gas emissions in Europe*, Denkstatt, Vienna, 2011.

- 25. Awareness and exchange of best practices on the implementation and enforcement of the essential requirements for packaging and packaging waste, Interim report, Bio Intelligence Service, Paris, 2011.
- 26. *Study on an increased mechanical recyling target for plastics.* Final Report for Plastics Recycling Europe, Bio Intelligence Service, Paris, 2013.
- 27. *How to boost plastics recycling and increase resource efficiency?* Strategy Paper of Plastics Recyclers Europe, Brussells, 2012.
- 28. Green paper on a European strategy on plastic waste in the environment, Brussels, 2013.
- 29. Assessment of impacts of options to reduce the use of single-use plastic carrier bags. Final Report, European Commission DG Environment, Brussells, 2011.
- Dalmijn, W. L., and de Jong, T. P. R. "Sorting systems for recycling and waste treatment," Voordracht VUB Brussells, Semin. *Het beheer van afvalstoffen*, Brussells, 2004.
- 31. Plastic Packaging. Recyclability by Design, Recoup Ltd., UK.
- 32. Foster, S. Domestic Mixed Waste Plastic Packaging Waste Management Options, WRAP, UK, 2012.
- 33. van Dongen, C., Dvorak, R., Kosior, E. *Design Guide for PET Bottle Recyclability*, UNESDA, EFBW, Brussels, 2011.
- 34. EV0422 Assessing the Environmental Impacts of Oxo-degradable Plastics Across Their Life Cycle, Department for Environment, Food and Rural Affairs, London, 2011.
- 35. Kozlowska, A., Kozlowski, M., Iwanczuk, A. Starch-based multiphase polymer materials, e-Polymers, 055, 2005.
- 36. *Bioplastics Opportunity for the Future*. PLASTICE project, Central Europe, 2013.
- Kozlowski, M. A., Macyszyn, J. Recycling of nanocomposites. In *Ecosustainable Polymer Nanomaterials for Food Packaging*, eds. C. Silvestre, S. Cimmino. CRC Press, 2013.

## Food Applications of Active and Intelligent Packaging: Legal Issues and Safety Concerns

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#### Abstract

Unlike traditional packaging, which must be totally inert, active packaging is designed to interact with the contents and/or the surrounding environment. Active packaging systems are successfully used to increase the shelf life of processed foods and can be categorized into adsorbing and releasing systems. Intelligent packaging is characterized by its ability to monitor the condition of packaged food or the environment by providing information about different factors during transportation and storage including time-temperature indicators, gas detectors, and freshness and/or ripening indicators. At the same time, advances in nanotechnology and the improvement of nanomaterials will enable the development of better and new active and intelligent packaging.

Until 2004, in Europe there was a lack of legislation for these kinds of packaging, decreasing their penetration in the EU market. To address the problem Regulation 1935/2004/EC and, more specifically, Regulation 450/2009/EC, set a new legal basis for their correct use, safety and marketing.

*Keywords:* Active packaging, intelligent packaging, regulation, food safety, food quality

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## 12.1 Introduction

The shelf life of packaged food depends on both the intrinsic nature of food and extrinsic factors. Intrinsic factors include pH, water activity (Aw), nutrient content, presence of antimicrobial compounds, redox potential, respiratory rate, and the biological structure; whereas extrinsic factors include storage temperature, relative humidity, and the surrounding gas composition. It follows that the primary purpose of food packaging is to protect the food against attack from oxygen, water vapor, ultraviolet light, and both chemical and microbiological contamination. However although the major functions of packaging are generally considered to be containment, protection, utility/convenience, communication/information and machinability, other minor functions can be underlined such as motivation, identification, resistance to processing, and reuse or recycle (Figure 12.1). Therefore, selection of appropriate packaging that is specified for foods, beverages or fresh produce should take into account all these functions [1].

Consumer demand for mildly preserved, minimally processed, easily prepared and ready-to-eat "fresher" foods—together with retail and distribution practices related to the globalization, new consumer product logistics, new distribution trends (e.g., internet shopping), automatic handling systems at distribution centers, and the stricter requirements regarding consumer health—pose major challenges for food quality and safety [2–4]. Moreover, there is a continual challenge to provide cost effective pack performance that satisfies the needs and wants of the user, with health and safety being of paramount importance. At the same time, it is important to minimize the environmental impact of products and the services required to deliver them. This challenge is continually stimulated by a number of key drivers—most notably, legislation and political pressure.

Active packaging (AP) and intelligent packaging (IP) technologies are being developed as a result of some of these driving forces [5,6]. Unlike traditional packaging, which must be totally inert, A&I packaging are designed to interact with the contents and/or the surrounding environment.

Active packaging refers to the incorporation of certain additives into packaging film or within packaging containers with the aim of maintaining and extending product shelf life. They include additives or freshness enhancers that are capable of scavenging oxygen; adsorbing carbon dioxide, moisture, ethylene and/or flavor/odor taints; releasing ethanol, sorbates, antioxidants and/or other preservatives; and/or maintaining temperature control [7]. The AP systems provide different solutions depending

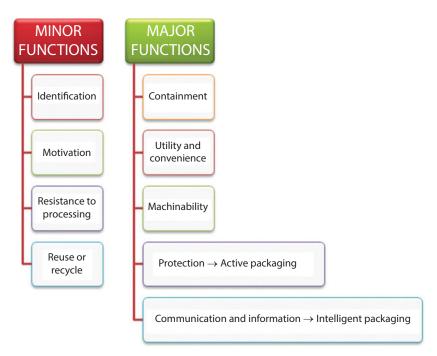


Figure 12.1 Packaging functions [8].

on the quality attribute that is to be preserved. For example, if oxidation of a food product has to be slowed down, the packaging must use an active system that contains an oxygen scavenger or antioxidants. If, however, the deterioration of the food is caused by moisture or condensation, the packaging may contain a moisture absorber.

Intelligent packaging is also an innovative concept that can be defined as a packaging system (or material) that uses either internal (e.g., metabolites) or external (e.g., temperature, gas, humidity) package environment as "information" to monitor the status of product quality for enhancing product safety, biosecurity and/or convenience or capable of tracking a product for automatic product identification and traceability [8]. Such packaging is characterized by its ability to monitor the condition of packaged food or the environment by providing information about different factors during transportation and storage.

It should be underlined, that AP is not synonymous with intelligent or smart packaging, which refers to packaging that senses and informs [7,9]. The IP devices are capable of sensing and providing information about the function and properties of packaged food and can provide assurances of pack integrity, tamper evidence, product safety and quality, and are being utilized in applications such as product authenticity, anti-theft and product traceability [7,9]. These IP devices include time-temperature indicators, gas sensing dyes, microbial growth indicators, physical shock indicators, and numerous examples of tamper proof, anti-counterfeiting and anti-theft technologies.

These systems can provide several benefits to the quality and safety of food and there is a strong view, underlined by the numbers on the global market of active and intelligent packaging, that they will be a tool with a high potential, covering both the more transparent communication to consumers and the need for the retail and food industry to better control the food production chain. However due to its deliberate interaction with the food and/or its environment, the migration of substances could represent a food safety concern, and most active and intelligent concepts that are on the market in the USA and Australia could not be introduced in Europe, due to more stringent EU legislation. In this regard, repealing of the EU Framework Directive for food contact materials 89/109/EEC, resulted firstly in the adoption of a Framework Regulation 1935/2004/EC [10] in which the use of active and intelligent packaging systems are now included. Only in 2009 can Regulation 450/2009/EC [11] be considered a specific measure that lays down rules ad hoc for active and intelligent materials and articles to be applied in addition to the general requirements established in Regulation 1935/2004/EC for their safe use. The aim of this chapter is to give an overview of the new legal issues set in Europe by the Framework Regulation 1935/2004/EC and, more specifically, by the Regulation 450/2009/EC. Moreover, safety issues and compliance will be also considered.

# 12.2 AP and IP: Main Characteristics and Applications

There are many different types of active and intelligent materials and articles [12,13]. Substances responsible for the active or intelligent function can be contained in a separate container, for instance in a small paper sachet, or they can be directly incorporated in the packaging material.

Concerning active packaging, they include additives or "freshness enhancers" that can participate in a host of packaging applications and by so doing, enhance the preservation function of the primary packaging system. The principal rewards that active food packaging brings are the efficient control of surface contamination where the microbial growth predominantly originates; protecting foodstuff with high water activity such as fish and seafood [14]; comparatively prolonged retention of antimicrobial activity [15]; extension of shelf life of foods by residual activity over time [16]; reducing the risk of pathogen development, i.e., log reduction [15]; restrain partial inactivation of active substances by product constituents cross-reaction [17]; controlled diffusion of bactericidal or bacteriostatic active agents; target specific microorganism population to provide higher safety [18]; a comparatively low use of preservative agents; simplification of the production process by combining the addition of preservatives and the packaging step; improving sensorial properties [19]; the ability to inhibit the germination of spores; applicable to ready-to-eat foodstuff [20]; imperative control of post-process contamination [21]; and above all, prevent economic loss and possible deaths due to foodborne infections.

Active packaging includes additives that are capable of scavenging or absorbing oxygen, carbon dioxide, ethylene, moisture and/or odor and flavor taints; releasing oxygen, carbon dioxide, moisture, ethanol, sorbates, antioxidants and/or other preservatives and antimicrobials; and/or maintaining temperature control (Figure 12.2). The wide diversity of active packaging devices have specific applications to individual food products through which the shelf life can be extended substantially, so long as the food's unique spoilage mechanisms are understood and controlled. Hence, an important objective is to design functional materials that include the active agent in their structure; then this active substance can act or be released in a controlled manner [22]. In this regard, recent data are available on either application to food industry of active packaging (Table 12.1) [23] or active packaging technologies (Table 12.2, Table 12.3) [23–26].

Intelligent packaging is packaging that in some way senses some properties of the food it encloses or the environment in which it is kept, and which is able to inform the manufacturer, retailer and consumer of the state of these properties (Table 12.4). Intelligent packaging is an extension of the communication function of traditional packaging, and communicates information to the consumer based on its ability to sense, detect, or record external or internal changes in the product's environment. Basically, there are two types of intelligent packaging: one based on measuring the condition of the package on the outside, the other measuring directly the quality of the food product, i.e., inside the packaging. In the latter case there is direct contact with the food or with the headspace and there is always the need for a marker indicative of the quality and/or safety of the packed food. Examples include time-temperature indicators (TTI), gas leakage indicators, ripeness indicators, toxin indicators, biosensors, and

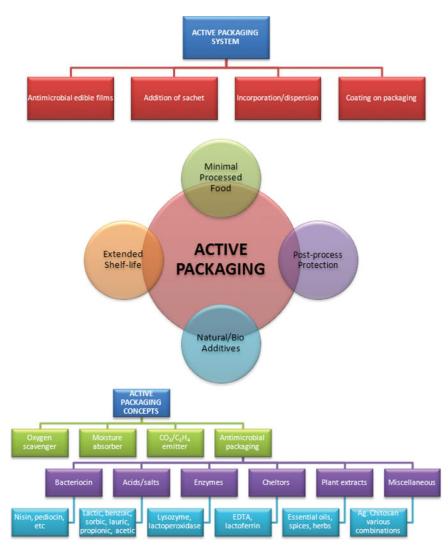


Figure 12.2 Active food packaging systems, concepts and application matrix [25].

radio frequency identification [4,9,23] (Table 12.5). Moreover, the active and intelligent materials and articles may be composed of one or more layers or parts of different types of materials, such as plastics, paper and board or coatings and varnishes.

The success of these new technologies is underlined by the economic dimension of the sector. In fact, the global market for advanced packaging solutions that includes active, controlled, intelligent packaging, and advanced packaging components was at US\$31.4 billion in 2011. This

Type of application	Foods
Oxygen scavengers	Ground coffee, tea, roasted nuts, potato chips, chocolate, fat poedered milk, powdered drinks, bread, tortillas, pizza, pizza crust, refrigerated fresh pasta, fruit tortes, cakes, cookies, beer, deli meats, smoked and cured meats, fish, cheese
Carbon dioxide absorbers	Ground coffee
Carbon dioxide emitters	Meat, fish
Moisture absorbers	Dry and dehydrated products, meat, poultry, fish
Ethylene scavengers	Kiwifruit, banana, avocados, persimmons
Ethanol emitters	Bread, cakes, fish
Antimicrobial releasing films	Dry apricots
Antioxidant releasing films	Cereals
Flavor absorbing films	Navel orange juice
Flavor releasing films	Ground coffee
Color containing films	Surimi
Anti-fogging films	Some fresh fruit and vegetable packages
Anti-sticking films	Soft candies, cheese slices
Light absorbers	Pizza, milk
Time-temperature indicators	Microwaveable pancake syrup, refrigerated pasta, deli items
Gas permeable/breath- able films	Ready-to-eat salads
Microwave susceptors	Ready-to-eat meals

 Table 12.1
 Applications of active packaging technologies [38].

value is expected to grow to nearly US\$44.3 billion in 2017 after increasing at a Compound annual growth rate (CAGR) of 5.8%. The market is still dominated by controlled packaging, which had sales of nearly US\$12.4 billion in 2011. The expected CAGR for controlled packaging is 6% from 2012 through 2017, resulting in a projected market value of US\$17.6 billion in 2017. Active packaging was next in market share in 2011 with nearly US\$8.8 billion in sales; the anticipated CAGR for this segment of advanced packaging is 5.2%, leading to a market value of US\$11.9 billion

Type of AP systemSubstances used and mode of action		
Oxygen scavengers	Enzymatic systems (glucose oxidase-glucose, alcohol oxidase-ethanol vapor) Chemical systems (powdered iron oxide, catechol, ferrous carbonate, iron-sulfur, sulfite salt-copper sulfate, photosensitive dye oxidation, ascorbic acid oxidation, catalytic conversion of oxygen by platinum catalyst)	
Carbon dioxide absorbing/emitting	Iron powder-calcium hydroxide, ferrous carbonate- metal halide	
Moisture absorbing	Silica gel, propylene glycol, polyvinyl alcohol, diato- maceous earth	
Ethylene absorbing	Activated charcoal, silica gel-potassium permanga- nate, Kieselguhr, bentonite, Fuller's earth, silicon dioxide powder, powdered Oya stone, zeolite, ozone	
Ethanol emitting	Encapsulated ethanol	
Antimicrobial releasing	Sorbates, benzoates, propionates, ethanol, ozone, peroxide, sulfur dioxide, antibiotics, silver-zeolite, quaternary ammonium salts	
Antioxidant releasing	BHA, BHT, TBHQ, ascorbic acid, tocopherol	
Flavor absorbing	Baking soda, active charcoal	
Flavor releasing	Many food flavors	
Color containing	Various food colors	
Anti-fogging and anti-sticking	Biaxially oriented vinylon, compression rolled ori- ented HDPE	
Light absorbing/ regulating	UV blocking agents, hydroxybenzophenone	
Monitoring	Time-temperature indicators	
Temperature controlling	Non-woven microperforated plastic	
Gas permeable/ breathable	Surface treated, perforated or microporous films	
Microwave susceptors	Metallized thermoplastics	
Insect repellant	Low toxicity fumigants (pyrethrins, permethrin)	

 Table 12.2 Examples of some currently known active packaging systems [12].

<b>TADIE 12.3</b> SOURE COMMENCIAR ACHIVE SYSTEMUS, LYPE OF PRESENTATION AND TADICTOR [20].	tills, type of f		1 1111CU1011 [20].	
Manufacturer	Country	Trade name	Scavenger mechanism	Packaging form
Mitsubishi Gas Chemical Co. Ltd	Japan	Ageless	Iron based	Sachets and labels
Toppan Printing Co. Ltd	Japan	Freshilizer	Iron based	Sachets
Toagosei Chem. Industry Co. Ltd	Japan	Vitalon	Iron based	Sachets
Nippon Soda Co. Ltd	Japan	Seagul	Iron based	Sachets
Finetec Co. Ltd	Japan	Sanso-Cut	Iron based	Sachets
Toyo Seikan Kaisha Ltd.	Japan	Oxyguard	Iron based	Plastic trays
Multisorb Technologies Inc.	USA	FreshMax	Iron based	Labels
		FreshPax	Iron based	Labels
		Fresh Pack	Iron based	Labels
Ciba Speciality Chemicals	USA	Shelf-plus	PET copolyester	Plastic film
Chevron Chemicals	USA	N/A	Benzyl acrylate	Plastic film
W. R. Grace Co. Ltd	USA	PureSeal	Ascorbate/metallic salts	Bottle crowns
Food Science Australia/Visy Industries	Australia	ZERO2	Photosensitive dye/organic compound	Plastic film
CMB Technologies	France	Oxbar	Cobalt catalyst	Plastic bottles
Standa Industries	France	ATCO	Iron based	Sachets
		Oxycap	Iron based	Bottle crowns
EMCO Packaging Systems	UK	ATCO	Iron based	Labels
Johnson Matthey Plc	UK	N/A	Platinum group	Labels
Bioka Ltd	Finland	Bioka	Enzyme based	Sachets
Alcoa CSI Europe	UK	O <sub>2</sub> -Displacer	Unknown	Bottle crowns

 Table 12.3
 Some commercial active systems, type of presentation and function [26].

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**Table 12.4** Examples of intelligent packaging applications for use within thefood industry [12].

Tamper evidence and pack integrity	Breach of pack containment
Indicators of product safety/quality	Time-temperature indicators (TTI's), gas sensing devices, microbial growth, pathogen detection
Traceability/anti-theft devices	Radio frequency identification (RFID) Labels, tags, chips
Product authenticity	Holographic images, logos, hidden design print elements, RFID

 Table 12.5
 Intelligent packaging systems for food applications [38].

Indicator	Principle/Reagents	Gives information about	Application
Time- temperature (external)	Mechanical Chemical Enzymatic	Storage Conditions	Foods stored under chilled and frozen conditions
Oxygen (internal)	Redox dyes pH dyes Enzymes	Storage conditions Package leak	Foods stored in MA packages
Carbon dioxide (internal)	Chemical	Storage conditions Package leak	MA or CA food packaging
Microbial growth (internal)	pH dyes All dyes reactingwith certain metabo- lites (volatiles or nonvolatiles)	Microbial quality of food	Perishable foods

in 2017. Advanced packaging components accounted for US\$6.5 billion of sales in 2011, and the market value for 2017 for this segment is expected to be at around US\$9.4 billion after rising at a 6.3% CAGR. The intelligent packaging sales were nearly US\$3.8 billion in 2011 and could approach US\$5.3 billion in 2017 with a CAGR of 5.6%. Because of the advantages it has in terms of marketing the product and its acceptance by the consumer, recently, a large number of companies sell this type of packaging. Some companies that sell active and/or intelligent packaging are shown in Table 12.6. Moreover, a number of portentous activities, such as collaborative

**Table 12.6** List of some companies that produce active and/or intelligent pack-aging [23].

Company	Web page	Country
Artibal	www.artibal.com	Spain
ATCO/Standa Industrie	www.atmospherecontrole.fr	France
BASF Group	www.basf.com	Germany
Bericap GmbH und Co. KG	www.bericap.com	Germany
Bio Fresh PKG	www.biofreshpkg.come	United States
Bioka LTD	www.bioka.fi	Finland
Ciba Inc. (BASF)	www.basf.com	Switzerland
Constar International Inc.	www.constar.net	United States
Cryolog S. A	www.cryolog.com	France
CSIRO	www.csiro.au	Australia
E-I-A Warenhandels GmbH	http://warenhandels.lookchem.com	Austria
Ethylene Control Inc.	www.ethylenecontrol.com	United States
Evert-Fresh Corporation	www.everfresh.com	United States
Freud Corporation	www.freud.co.jp	Japan
Grace Darex Packaging Technologies	www.gracedarex.com	United States
Honeywell International Inc.	www51.honeywell.com/honeywell	United States
Hsaio SUNG Non-Oxygen Chemical Co., LTD	www.o-buster.com	Taiwan
Humidipak, Inc.	www.humidipak.com	United States
Infratab, Inc.	www.infratab.com	United States
Inline Packaging LLC.	www.inlinepkg.com	United States
KonteK (S. R. L.) Tecnologie Della Conservazione Ortofrutticola		Italy
M&G Finanziaria s.r.l.	www.gruppomg.com	Italy
Mitsubushi Gas Chemical	www.mgc.co.jp	Japan
Multisorb Technologies	www.multisorb.com	United States
PEAK fresh	http://peakfresh.com	Australia
Powdertech, Co. Ltd.	www.powdertech.com	Japan
Repsol	www.repsol.com	Spain
ScentSational Technologies, LLC	www.scentsationaltechnologies.com	United States
Sealed Air Corporation	www.sealedair.com	United States

Company	Web page	Country
Sirane Ltd	www.irane.co.uk	United Kingdom
Sud-Chemie AG	ww.sud-chemie.com	Germany
Techmer PM	www.techmerpm.com	United States
Telatemp Corporation	www.telatemp.com	United States
Tempra Technology and Crown Holdings	www.tempratech.com	United States
Toppan Printing Co.	www.toppan.co.jp	Japan
Toxin Alert	www.toxinalert.com	Canada
Toyo Seikan Kaisha, Ltd	www.toyo-seikan.co.jp	Japan
Tri-Seal (Tekni-Plex)	www.tri-seal.com	United States
UOP LLC.	www.uop.com	United States
Valspar Corporation	www.valsparglobal.com	United States

efforts and new product development in the Asia-Pacific region as well as in the European and North American markets, were witnessed.

## 12.2.1 Nanotechnology

The invention of nanotechnology and its implementation in food products and active/smart packaging has been approved due to its enabling nature. Nanoscience is "the study of phenomena and manipulation of materials at atomic, molecular, and macromolecular scales (0.2–100 nm), where properties differ significantly from those at a larger scale," whereas nanotechnology is "the design, characterisation, production, and application of structures, devices, and systems by controlling the shape and size at the nanometre scale" [27]. The US definition is that "nanotechnology is the understanding and control of matter at dimensions of roughly 1 to 100 nanometers, where unique phenomena enable novel applications." Encompassing nanoscale science, engineering, and technology, nanotechnology involves imaging, measuring, modeling, and manipulating matter at this length scale [28].

Nanotechnology has the potential to transform food packaging materials in the future. Such nanoscale innovation could potentially introduce many amazing new improvements to food packaging in the forms of barrier and mechanical properties, detection of pathogens, and smart and active packaging with food safety and quality benefits. The nanolayer of aluminum that coats the interior of many snack food packages is one common example of the role that nanotechnology already plays in food packaging. Nanomaterials are abundant in nature and numerous techniques are available to fabricate various nanomaterials. Nanoparticles can be produced top down from larger structures by grinding, use of lasers, and vaporization followed by cooling. Alternately, bottom-up methods are commonly used for synthesis of complex nanoparticles. These methods include solvent extraction/evaporation, crystallization, self-assembly, layer-by-layer deposition, microbial synthesis, and biomass reactions [25]. All of these are being researched for potential application in food packages in the future.

Packaging that incorporates nanomaterials can be "smart/intelligent," which means that it can respond to environmental conditions or repair itself or alert a consumer to contamination and/or the presence of pathogens. Some of the applications associated with nanotechnology include improved taste, color, flavor, texture and consistency of foodstuffs, increased absorption and bioavailability of food or food ingredients (nutrients), and the development of new food-packaging materials with improved mechanical, barrier and antimicrobial properties [29–31]. One group of nanomaterials at the forefront of food packaging development is nanocomposites; improvements in fundamental characteristics of food-packaging materials such as strength, barrier properties, antimicrobial properties, and stability to heat and cold are in fact being achieved using nanocomposite materials [32].

Self-healing packaging materials use nano/micro-encapsulated repairing agents. Small amounts of an encapsulated "healing agent" will be released by crack propagation or other triggering mechanism, which have been incorporated into polymeric coatings. The substitution of flexible polyolefin layers with novel, thin, functional polymer coatings in the production of paperboard packaging entails the risk of deteriorated barrier and mechanical properties. However, tiny capsules with a hydrophobic core surrounded by a hydrophobically modified polysaccharide membrane reasonably enhanced the packaging functionality. The results showed a reduced tendency for deteriorated barrier properties and local blockage of cracks formed upon creasing. The self-healing mechanism engages the break of tiny capsules local to the applied stress, with subsequent release of the core material. Fracture propagation is hampered by plasticization of the underlying coating layer, while the augmented hydrophobicity assists in sustaining the barrier characteristics [33].

Other applications include carbon nanotubes or nanosensors. The first are cylinders with nanoscale diameters that can be used in food packaging

to improve its mechanical properties, although it was recently discovered that they may also exert powerful antimicrobial effects [34], while nanosensors could be used to detect chemicals, pathogens, and toxins in foods [35].

Security of the food supply may possibly be enhanced by making "pathogen-repulsive" surfaces or packaging materials that change color in the incidence of injurious microorganisms or toxins [36]. Moreover, nanoscale technologies also are in development to improve traceability and for monitoring the condition of food during transport and storage.

## 12.3 Legal Issues

## 12.3.1 Definitions

For the purpose of this chapter, the definitions laid down in Regulation (EC) No 1935/2004 and in Regulation (EC) No 450 /2009 shall apply.

- "Active materials and articles" means materials and articles that are intended to extend the shelf life or to maintain or improve the condition of packaged food. They are designed to deliberately incorporate components that would release or absorb substances into or from the packaged food or the environment surrounding the food (Regulation (EC) No 1935/2004 Article 2.2.a and Regulation (EC) No 450/2009 Article 3.a). This definition of active materials and articles is interpreted as including all materials and articles that are designed to deliberately interact with food and/or the food surrounding environment, and bring about change in their composition or characteristics.
- "Intelligent materials and articles" means materials and articles which monitor the condition of packaged food or the environment surrounding the food. (Regulation (EC) No 1935/2004 Article 2.2.b and Regulation (EC) No 450/2009 Article 3.b);
- "Component" means an individual substance or a combination of individual substances which cause the active and/ or intelligent function of a material or article, including the products of *in situ* reaction of these substances. It does not include the passive part, such as the material they are added to or incorporated into. (Regulation (EC) No 450/2009

Article 3.c). The component might be the individual active substance only. The component can also be a combination or group of substances that, e.g., when the active or intelligent function implies interaction between different substances leading to an enhancement of the function or the generation of new substances responsible for the active and intelligent function.

- "Functional barrier" means a barrier consisting of one or more layers of food contact materials which ensures that the finished material or article complies with Article 3 of Regulation (EC) No 1935/2004 and with Regulation (EC) No 450/2009. This barrier is a layer within the food contact materials or articles preventing the migration of substances from behind that barrier into the food. The maximum tolerated migration level is 0,01 mg substance /kg food for a substance. This migration limit is applicable to a group of substances if they are structurally and toxicologically related, in particular isomers or substances with the same relevant functional group; it also includes possible set-off transfer. This limit shall always be expressed as a concentration in foods. If it is demonstrated that the packaging material or a layer acts as a functional barrier to migration then nonauthorised substances can be used in the layer (s) behind the barrier (not on the food contact side) provided they don't fall under one of the following categories:
  - Substances that are mutagenic, carcinogenic or toxic to reproduction should not be used in food contact materials or articles without previous authorisation and are therefore not covered by the functional barrier concept.
  - New technologies that engineer substances in particle size that exhibit chemical and physical properties that significantly differ from those at a larger scale, for example, nanoparticles, should be assessed on a case-bycase basis as regards their risk until more information is known about such new technology. Therefore, they are not covered by the functional barrier concept. This should be demonstrated in the declaration of compliance and the supporting documentation [(EC) No 450/2009 Article 13 and Annex II (10)].
- "Releasing active materials and articles" are those active materials and articles designed to deliberately incorporate

components that would release substances into or onto the packaged food or the environment surrounding the food. (Regulation (EC) No 450/2009 Article 3.e);

- "Released active substances" are those substances intended to be released from releasing active materials and articles into or onto the packaged food or the environment surrounding the food and fulfilling a purpose in the food. (Regulation (EC) No 450/2009 Article 3.f);
- "Active and/or intelligent substance" means a substance which contributes to the active and/or intelligent function;
- "Passive parts" means all material(s) and article(s) into which the component is added or incorporated (such as the container and the primary packaging into which that component is placed or the primary packaging material into which it is incorporated).

## 12.3.2 Regulation (EC) No 1935/2004 and Regulation (EC) No 450 /2009

The regulatory systems for active packaging employed in the United States and Europe is apparently similar, but each has its own special set of exemptions. In brief, the US approach considers that "the dose makes the poison" so that toxicological justification is not needed, while the European approach starts from the principle that there must be toxicological data on all substances regardless of the level of anticipated exposure [37,38].

In Europe, the Framework Regulation (EC) 1935/2004 allows the introduction of active and intelligent packaging on the European market. This Regulation states that food contact materials shall not transfer constituents to food in quantities, which could endanger human health, bring about an unacceptable change in the composition and bring about deterioration in organoleptic characteristics thereof (Article 3). The Regulation provides specific requirements for active and intelligent materials and articles (Article 4) and includes the following provisions:

- Active materials and articles may bring about changes in the composition or organoleptic characteristics of food on condition that the changes comply with the food legislation.
- Substances deliberately incorporated into active materials and articles to be released into the food or the environment

surrounding the food shall be authorised and used in accordance with the relevant EU provisions applicable to food.

- Active materials and articles shall not bring about changes in the composition or organoleptic characteristics of food, for instance by masking the spoilage of food, which could mislead consumers.
- Intelligent materials and articles shall not give information about the condition of the food which could mislead consumers.
- Active and intelligent materials and articles already brought into contact with food shall be adequately labeled to allow identification by the consumer of non-edible parts.
- Active and intelligent materials and articles shall be adequately labeled to indicate that the materials or articles are active and/or intelligent.
- Commission Regulation (EC) No 450/2009 is the specific measure under the Framework Regulation that regulates active and intelligent materials and articles. This Regulation includes additional provisions:
  - The individual substance or group/combination of substances which make up the active or intelligent component should be safe and comply with the requirements in the Framework Regulation (EC) No 1935/2004 and the Regulation (EC) No 450/2009.
  - Substances should undergo a safety assessment by EFSA before they are authorised for use. It is mentioned that the substances responsible for the active and intelligent functions can either be contained in separate containers (e.g. oxygen absorbers in small sachets) or be directly incorporated in the packaging material (e.g. oxygen absorbing films). Moreover, the materials may be composed of one or more layers or parts of different types of materials, such as plastics, paper, and board as well as coatings and varnishes. Only the active and intelligent "components" should be subjected to authorization. Safety evaluation does not apply to substances used behind a functional barrier as defined by article 3 of Regulation (EC) No 450/2009. Substances behind such a barrier will not, by definition, migrate in amounts which could endanger human health or bring about unacceptable changes in the composition of the food or of its organoleptic properties.

Consequently, these active and intelligent substances do not need a safety evaluation and are also outside the scope of Regulation (EC) No 450/2009. However, this functional barrier concept does not apply to substances in nanoparticulate form which should be assessed on a case by case basis (article 5(2)(c)ii of regulation No 450/2009).

- A Union list of substances or group/combination of substances to be used in active and intelligent components should be drawn up following risk assessment of these substances by EFSA; the deadline for submitting applications to establish the EU positive list is not over yet. In some cases, restrictions may be proposed by the EFSA on a group of substances especially when the active or intelligent function implies interactions between different substances. The Union list will include:
  - the identity: name, synonym name, CAS No, EC No, particle size, when relevant, composition, other specifications
  - the function
  - the reference number
  - the conditions of use of the substance or the component
  - the restrictions and/or specifications of the use of the substance
  - the conditions of use of the material and article to which the substance or component is added or into which it is incorporated
- Substances released from active releasing materials should comply with any restrictions in the existing food law (e.g. as authorised food additives) thus complying with the safety requirement. They do not need to be listed in the Community list. They shall be used in full compliance with the relevant Community and national provisions applicable to food, and shall comply with the provisions of Regulation (EC) No 1935/2004 and its implementing measures. The same shall apply to substances which are incorporated in active materials and articles by techniques such as grafting and immobilisation, in order to have a technological effect in the food.

- The overall migration from active releasing materials can exceed the overall migration limits described in EU or national legislation as long as the levels transferred to the food comply with restrictions in the existing food law (e.g. as authorised food additives). The transfer of these active substance/substances should not be included in the calculation of the overall migration limit (OML).
- As well as complying with the Framework Regulation the passive parts of the active and intelligent packaging materials must also comply with the rules applicable to the same materials and articles when they do not contain the active component, such as the Plastics Regulation (EU) No 10/2011 [39]. For materials such as paper and board for which the specific requirements are not regulated at EU level existing national legislation should be applied.
- Intelligent systems that are on the non-food contact surface of the package can be separated from the foodstuff by a functional barrier, i.e. a barrier to any migration. If it is demonstrated that the packaging material acts as a functional barrier to migration then non-authorised substances can be used providing they meet specific criteria defined in the Regulation.

#### 12.3.3 Labeling Requirements

Articles 4(d) and 11 of (EC) No 450/2009 specify that active and intelligent materials should be labeled. For example, to avoid that the content of sachets are perceived as edible, these should be labeled as non-edible.

Articles 12 and 13 specify that information should be provided throughout the packaging chain as well as to the consumer to ensure the correct use of these materials and articles. Active materials and articles which are not yet in contact with food when placed on the market, e.g., a packaging containing an antioxidant to be released in the food, are to be accompanied by information on the permitted use or uses and other relevant information such as the name and maximum quantity of the antioxidant released by the active component. In this way the food business operators who use these materials and articles are enabled to comply with any other EU or national provisions applicable to food such as the permitted level of the antioxidant in the food. The labeling of food packed in active materials and articles that contain substances to be released into the food shall be performed according to the relevant EU labeling provisions. Released active substances are considered as ingredients within the meaning of Article 6(4)(a) of Directive 2000/13/EC [40]. Food additives remain subject to the general labeling obligations as provided for in Directive 2000/13/EC of the European Parliament and of the Council of 20 March 2000 on the approximation of the laws of the Member States relating to the labeling, presentation and advertising of foodstuffs.

## 12.3.4 Declaration of Compliance

Article 16 of the Framework Regulation (EC) No 1935/2004 provides that materials and articles are to be accompanied by a written declaration of compliance attesting that they comply with the rules applicable to them. Active and intelligent materials and articles, whether or not they are in contact with food, or the components intended for the manufacturing of those materials and articles or the substances intended for the manufacturing of those components shall be accompanied by a written declaration at the marketing stages other than at the point of sale to the final consumer. Annex II of Commission Regulation (EC) No 450/2009 contains the required information. When the material or article also has to meet the requirements of other food contact materials legislation, for example under (EU) No 10/2011, then the declaration of compliance also has to contain that necessary information as required by that legislation.

## 12.4 Dossier Submission and EFSA Safety Assessment

The community list of authorized substances that can be used to manufacture an active or intelligent component of active and/or intelligent materials and articles, shall be established after the European Food Safety Authority (EFSA) has performed a risk assessment and has issued an opinion on each substance. In particular, the risk assessment of nanoparticles has to be performed on a case-by-case basis. This is necessary because data on toxicity and oral exposure of nanoparticles are currently extremely limited. In addition, the small size of many nanoparticles causes them to take on unique chemical and physical properties that are different from their macroscale chemical counterparts. The large surface area of nanoparticles allows a greater contact with cellular membranes, as well as greater capacity for absorption and migration [41]. This implies that their toxicokinetic and toxicity profiles cannot be extrapolated from data on their equivalent non-nanoforms. Exposure to nanoparticles is likely to occur through dermal contact with the packaging material, or ingestion due to the leakage to foodstuff [41]; also inhalation of nanoparticles is of particular concern [42]. In addition, nanoparticles may migrate into foods from recycled packaging produced from material that contains nanoparticles. Also, nanoparticles may be released into the environment and enter the food chain indirectly [43].

After reviewing the document and in order to guarantee that the foods in contact with active and intelligent materials and articles are safe, the EFSA will, where appropriate, issue opinion, recommendations, specifications or restrictions on the substance(s) or group of substances incorporated in active or intelligent food contact materials and articles and when necessary, special conditions of manufacture and use for these substances and/or the materials and articles in which they are incorporated. After a positive evaluation, the authorization is valid for 10 years (renewal necessary) (Figure 12.3) and it is not "general" but is only for the petitioner ("Authorisation holder").

The EFSA safety assessment process will focus on the risks related to the dietary exposure to chemicals due to:

- The migration of the active and/or intelligent substance (s);
- The migration of their degradation and/or reaction products;
- Their toxicological properties.

The dossier submitted by the applicant shall include all relevant information enabling the EFSA to perform a complete evaluation. It should be noted that efficacy of active and/or intelligent material and article and most importantly any technical parameters and restrictions needed to ensure efficacy will be considered only when relevant for safety evaluation. The EFSA evaluation cannot be considered as proof of the technical efficacy of active and/or intelligent material and article. It should be noted that these guidelines do not include any consideration of environmental aspects such as persistence in the environment, ecological impact of food contact materials constituents and their fate after the food contact material has been submitted to waste disposal treatment.

The dossier shall be composed of three sections:

- a) The summary document;
- b) The administrative part;
- c) The technical part (technical dossier).

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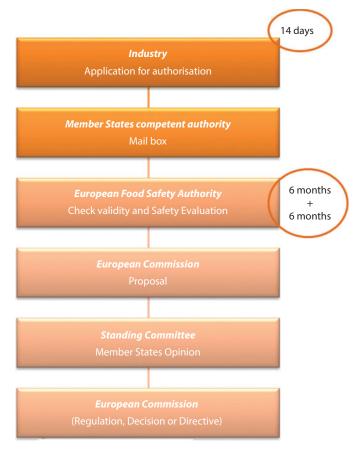


Figure 12.3 Authorization procedure as defined by Reg. 1935/2004 EC [38].

The summary document should contain a summary of all information provided in the technical dossier (TD) and the safety evaluation, including:

- The principle and target function of the active or intelligent material or article;
- The identity and relevant physical and chemical characteristics of the active and/or intelligent substance(s);
- The manufacturing process of the active or intelligent substance(s), the type(s) of materials in which the substance(s) can be added or incorporated into and manufacturing conditions of the active and/or intelligent materials and articles;

- The intended use of the active and/or intelligent materials or articles with respect to the types of foods and the conditions of time and temperature of use;
- The existing authorization in EU Member States and other countries;
- The migration data;
- The toxicological data.

In the administrative part, the data supplied shall identify the legal entities and the business involved, as well as the person in charge of the application.

The technical dossier should start with an overview of the application relating with the composition, structure and working principle of the active or intelligent material or article. The target function, the active and intelligent substance(s) and passive parts of the material or article, their functions and other information necessary for understanding their mode of action such as intended migration or reaction, as well as the importance of usage conditions should be presented in a synthetic and comprehensive way.

In the case of interactions among substances responsible for the active or intelligent function, all the relevant information, for all these substances should be submitted in the dossier.

The identity of the active or intelligent substance(s) should then provide all relevant information on the identity of the active or intelligent substance(s) and its (their) impurities giving respective chemical name (IUPAC), CAS registry number, synonyms and trade names, abbreviation, molecular weight, molecular and structural formula abd spectroscopic. If a mixture, also the proportion of each constituent in the mixture must be given.

Then, all relevant information on the physical and chemical properties of the active and intelligent substance(s), such as physical state, melting point, boiling point, solubility, octanol/water partition, stability, decomposition temperature, reactivity and hydrolysis shall be provided.

Information on any intended or potential unintended reaction or breakdown products originating for instance during the manufacturing process, the storage or the use of active and intelligent substance(s) including, if any, reactions with passive parts of packaging materials, substances of the food surrounding atmosphere or natural compounds of the food shall also be provided.

In the section of the manifacturing process a detailed description should be given of:

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- The manufacturing process of the active or intelligent substance(s);
- The nature of the passive parts and;
- The process of incorporation of the active and/or intelligent substances in the finished material or article;
- The types of the food contact material(s);
- The maximum percentage of the active or intelligent substance(s) in the food contact material.

The applicant shall identify any possible reaction and/or degradation products under the conditions of the manufacturing processes.

Moreover, information shall be provided on the range of food categories that active and intelligent materials and articles are intended/recommended to be used with. Intended and worst case conditions of use (time, temperature, surface/volume ratio or anything of relevance for the safety evaluation) of active or intelligent materials and articles with those foods should be given. In this section the applicant shall also provide data relevant to the efficacy of the active and/or intelligent materials and articles for the intended use.

All relevant information on the legal status of the active and intelligent substances in respect to the EU and/or national legislation as well as information concerning authorization in other countries shall be also provided. It should be indicated whether the material and article has been authorized as such (the same active or intelligent substance(s) for the same passive parts and same usage conditions) or a similar material or article (material or article having similar principle and function, i.e., similar active or intelligent substance(s), passive parts and usage conditions

Migration data of active and/or intelligent substances and, if any, impurities, reaction products and degradation products, should be provided using where appropriate conventional migration tests, as described in the Directive 82/711/EEC [44] or dedicated migration/evaluation tests in foods or simulants with demonstrated adequacy for the intended/recommended conditions of use. Alternatively, calculations based on worst case transfer scenarios or recognized mathematical migration models [45] may be used including any assumptions made. Validated analytical methods for the determination of the substances and if relevant their degradation and reaction products in food or food simulants and/or in the final material should be given in detail except where the analytical methods used are well established and may be given by reference only.

If known, estimates of exposure to the migrating substances from other sources should be provided. Finally, toxicological data on each substance and if relevant on its/their degradation products and any identified reaction byproducts, should be provided. As a general principle, the extent of toxicological studies needed will be dependent on the level of exposure through migration. The greater the exposure, the more toxicological information will be required. The same tiered approach as described in the guidelines of the Scientific Committee on Food [46] for the presentation of an application for safety assessment of a substance to be used in food contact materials prior to its authorization has to be followed.

In cases where a substance is already authorized in food or food contact materials Community legislation or evaluated by the SCF or EFSA, a reference to that legislation or evaluation of the substance should in first instance be provided instead of the above toxicological data.

## 12.5 Conclusions

Bioactive packaging is progressively more experimented upon because it is believed to have a significant potential in improving food safety and prolonging the shelf life of food products. It follows that a bright future may be anticipated for active and intelligent packaging. However, despite long-time commercial use without particular safety concerns, few examples of these new technologies were present in Europe due to the lack of legislation. To solve the problem the Regulation 1935/2004/EC and new Regulation 450/2009/EC pose a new basis for the general requirements and specific safety and marketing issues related to active and intelligent packaging in the EU. Both regulations seem to be necessary and helpful because they both fit perfectly with the food safety strategy, involving an improved level of food safety and transparency to consumers. In fact, it should be considered that the complexity of systems introduce many variables into risk assessment. Pouches/sachets may introduce new migration products and lead to interactions between active agents and other packaging materials. The development and validation of migration tests to reliably detect and measure new migration products could represent a serious challenge, as well as the risk assessment for nanomaterials. In this context, further research on active food packaging materials is necessary not only to reveal the mechanisms of action of existing systems, but also to develop novel efficient active agents. Current trends suggest that active packaging will generally incorporate micro- or nanotechnology to accomplish more effective and efficient improvement. Parallel tests with diverse foods will be indispensable before we reach the ideal combination, working equally well for a majority of foods.

Anyway, despite the hurdles that have to be overcome in the near future, there is a strong view that active and intelligent packaging will be a technical tool in the market with both high potential and more transparent communication with the consumer.

# References

- 1. Robertson, G. L. *Food Packaging: Principles and Practice*, 3rd ed. Boca Raton: CRC Press, 2012.
- 2. Vermeiren, L., Devlieghere, F., van Beest, M., de Kruijf, N., Debevere, J. Development in the active packaging of foods. *Trends Food Sci Tech* 10:77–86, 1999.
- 3. Sonneveld, K. What drives (food) packaging innovation? *Packag Technol Sci* 13:29–35, 2000.
- 4. Yam, K. L., Takhistov, P. T., Miltz, J. Intelligent packaging: Concepts and applications. *J Food Sci* 70:R1–R10, 2005.
- 5. Suppakul, P., Miltz, J., Sonneveld, K., Bigger, S. W. Active packaging technologies with an emphasis on antimicrobial packaging and its applications. *J Food Sci* 68:408–420, 2003.
- 6. Nopwinyuwong, A., Trevanich, S., Suppakul, P. Development of a novel colorimetric indicator label for monitoring freshness of intermediate-moisture dessert spoilage. *Talanta* 81:1126–1132, 2010.
- Day, BPF. Active packaging of food. In *Smart Packaging Technlogies for Fast Moving Consumer Goods*, eds. J. Kerry, P. Butler, pp. 1–18. West Sussex: John Wiley & Sons Ltd., 2008.
- Suppakul, P. Intelligent packaging. Part VII: Trends in frozen food packing. In *Handbook of Frozen Food Processing and Packaging*, 2nd ed. D.-W. Sun, pp. 837–860. Boca Raton: CRC Press, 2012.
- 9. Summers, L. *Intelligent Packaging*. London: Centre for Exploitation of Science and Technology, 1992.
- The Commission of the European Communities. Regulation (EC) No. 1935/2004 of the European Parliament and of the Council of 27 October 2004 on materials and articles intended to come into contact with food and repealing Directives 80/590/EEC and 89/109/EEC. Official Journal of the European Union, L338, 2004.
- The Commission of the European Communities. Commission Regulation (EC) No. 450/2009 of 29 May 2009 on active and intelligent materials and articles intended to come into contact with food. *Official Journal of the European Union*, L135, 2009.
- 12. Ozdemir, M., Floros, J. D. Active food packaging technologies. *Crit Rev Food Sci Nutr* 44:185–193, 2004.

- Rooney, M. L. Introduction to active food packaging technologies. In Innovations in Food Packaging, ed. J. H. Han, pp. 63–79. Oxford: Elsevier Academic Press, 2005.
- 14. Millette, M., Le Tien, C., Smoragiewicz, W., Lacroix, M. Inhibition of *Staphylococcus aureus* on beef by nisin-containing modified alginate films and beads. *Food Control* 18:878–884, 2007.
- Scannell, A. G. M., Hill, C., Ross, R. P., Marx, S., Hartmeier, W., Arendt, E. K. Development of bioactive food packaging materials using immobilised bacteriocins Lacticin 3147 and Nisaplin. *Int J Food Microbiol* 60:241–249, 2000.
- 16. Mauriello, G., Ercolini, D., La Storia, A., Casaburi, A., Villani, F. Development of polythene films for food packaging activated with an antilisterial bacteriocin from Lactobacillus curvatus 32Y. *J Appl Microbiol* 97:314–322, 2004.
- 17. Mauriello, G., De Luca, E., La Storia, A., Villani, F., Ercolini, D. Antimicrobial activity of a nisin-activated plastic film for food packaging. *Lett Appl Microbiol* 41:464–469, 2005.
- Quintavalla, S., Vicini, L. Antimicrobial food packaging in meat industry. *Meat Sci* 62:373–380, 2002.
- 19. Vermeiren, L., Devlieghere, F., Debevere, J. Effectiveness of some recent antimicrobial packaging concepts. *Food Addit Contam* 19:163–171, 2002.
- Janes, M. E., Kooshesh, S., Johnson, M. G. Control of Listeria monocytogenes on the surface of refrigerated, ready-to-eat chicken coated with edible zein film coatings containing nisin and/or calcium propionate. *J Food Sci* 67:2754– 2757, 2002.
- Kristo, E., Koutsoumanis, K. P., Biliaderis, C. G. Thermal, mechanical and water vapor barrier properties of sodium caseinate films containing antimicrobials and their inhibitory action on Listeria monocytogenes. *Food Hydrocolloid* 22:373–386, 2008.
- 22. Coma, V. Bioactive packaging technologies for extended shelf life of meatbased products. *Meat Sci* 78:90–103, 2008.
- 23. Pereira de Abreu, D. A., Cruz, J., Paseiro Rosada, P. Active and intelligent packaging for the food industry. *Food Rev Int* 28:146–187, 2012.
- 24. Joerger, R. D. Antimicrobial films for food applications: a quantitative analysis of their effectiveness. *Packag Technol Sci* 20:231–273, 2007.
- 25. Imran, M., Revol-Junelles, A. M., Martyn, A., Arab Tehrany, E., Jacquot, M., Linder, M., Desobry, S. Active food packaging evolution: transformation from micro- to nanotechnology. *Crit Rev Food Sci Nutr* 50:799–821, 2010.
- Day, B. P. F. Active packaging. In *Food Packaging Technology*, eds. R. Coles, D. McDowell, M. J. Kirwan, pp. 283–302. Oxford (UK): Blackwell Publishing Ltd, 2003.
- 27. Royal Society and Royal Academy of Engineering, Nanoscience and nanotechnologies: *Opportunities and uncertainties*, 2004, http://www.nanotec.org. uk/finalreport. pdf, 2008.
- NNI, National Nanotechnology Initiative (2001), http://www.nano.gov/., 2008.

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- 29. Chawengkijwanich, C., Hayata, Y. Development of TiO<sub>2</sub> powder-coated food packaging film and its ability to inactivate *Escherichia coli in vitro* and in actual tests. *Int J Food Microbiol* 123:288–292, 2008.
- Rhim, J. W., Hong, S. I., Park, H. M., Ng, P. K. W. Preparation and characterization of chitosan-based nanocomposite films with antimicrobial activity. J Agr Food Chem 54:5814–5822, 2006.
- Rhim, J. W., Ng, P. K. W. Natural biopolymer-based nanocomposite films for packaging applications. *Cr Rev Food Sci* 47:411–433, 2007.
- Lagarón, J. M., Busolo, M. A. Multifunctional nanoclays for food contact applications. In *Multifunctional and Nanoreinforced Polymers for Food Packaging*, ed. J. M. Lagarón, pp. 31–42. Cambridge: Woodhead Publishing Ltd, 2011.
- Andersson, C., Järnström, L., Fogden, A., Mira, I., Voit, W., Zywicki, S., Bartkowiak, A. Preparation and incorporation of microcapsules in functional coatings for self-healing of packaging board. *Pack Technol Sci* 22:275–291, 2009.
- Kang, S., Pinault, M., Pfefferle, L. D., Elimelech, M. Single-walled carbon nanotubes exhibit strong antimicrobial activity. *Langmuir* 23:8670–8673, 2007.
- Liu, Y., Chakrabartty, S., Alocilja, E. Fundamental building blocks for molecular biowire based forward error-correcting biosensors. *Nanotechnology* 18:1–6, 2007.
- Moraru, C. I., Panchapakesan, C. P., Huang, Q., Takhistov, P., Liu, S., Kokini, J. L. Nanotechnology: A new frontier in food science. *Food Technol* 57:24–29, 2003.
- Dainelli, D., Gontard, N., Spyropoulos, D., Zondervan-van den Beuken, E., Tobback, P. Active and intelligent food packaging: Legal aspects and safety concerns. *Trends Food Sci Tech* 19:99–108, 2008.
- Restuccia, D., Spizzirri, U. G., Parisi, O. I., Cirillo, G., Curcio, M., Iemma, F., Puoci, F., Vinci, G., Picci, N. New EU regulation aspects and global market of active and intelligent packaging for food industry applications. *Food Control* 21:1425–1435, 2010.
- 39. The Commission of the European Communities. Commission Regulation (EC) No. 10/2011 of 14 January 2011 on plastic materials and articles intended to come into contact with food. *Official Journal of the European Union*, L12, 2011.
- 40. The Commission of the European Communities. Directive 2000/13/EC of the European Parliament and of The Council of 20 March 2000 on the approximation of the laws of the Member States relating to the labelling, presentation and advertising of foodstuffs. *Official Journal of the European Union*, L109, 2000.
- 41. Li, S. D., Huang, L. Pharmacokinetics and biodistribution of nanoparticles. *Mol Pharmaceut* 5:496–504, 2008.
- 42. Carlson, C., Hussain, S. M., Schrand, A. M., Braydich-Stolle, K. L., Hess, K. L., Jones, R. L., Schlager, J. J. Unique cellular interaction of silver

nanoparticles: Size-dependent generation of reactive oxygen species. *J Phys Chem B* 112:13608–13619, 2008.

- 43. Hoet, P. H., Brüske-Hohlfeld, I., Salata, O. V. Nanoparticles: Known and unknown health risks. *J Nanobiotechnology* 2:12–26, 2004.
- 44. The Commission of the European Communities. Directive 82/711/EEC of the Council of 18 October 1982 laying down the basic rules necessary for testing migration of constituents of plastic materials and articles intended to come into contact with foodstuffs. *Official Journal of the European Union*
- 45. The Commission of the European Communities. Directive No 2002/72/EC of the Commission relating to plastic materials and articles intended to come into contact with foodstuffs. *Official Journal of the European Union*, L 220, 2002.
- 46. The Commission of the European Communities. Guidelines of the Scientific Committee on food for the presentation of an application for safety assessment of a substance to be used in food contact materials prior to its authorization. SCF/CS/PLEN/GEN/100 Final. http://ec.europa.eu/food/fs/sc/scf/ out82\_en.pdf, 2001.

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