

## 10

# Membranes for Food Packaging

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### 10.1

#### Introduction

The development of new materials for food packaging is a challenge that involves scientific and technological competences. Consumer needs and socioeconomic problems are the most important driving forces of this process that has, as ultimate goal, the delivery of high-quality and safe food products to the consumer in an efficient manner [1].

All the materials used as food contact materials (FCM) must have specific and distinctive characteristics. The preliminary requirement is the safety of material. This means that the possible migration of undesirable packaging constituents into the food has to be well known and controlled. The matters of inertness of FCM and packaging reliability are in the domain of law in all the developed countries, where nowadays exist very huge detailed and generally severe regulations on this topic. Other complementary and essential performances concern all those physical and chemical properties that give specific behavior to the material under conditions of use. For example, physical properties such as gas permeation through package walls, mechanical resistance to environmental stress, sealability, and so on, are very important and useful both for controlling the package-fabrication process and to design the food package able to maintain and guarantee the quality and safety of the product during its shelf life. In fact, environmental factors such as humidity, oxygen, light, and so on (which can induce degradation reactions during storage) should be strictly controlled and in some cases modulated by the packaging material.

Synthetic polymers are the materials of choice for many food-packaging applications. They have molecular weights typically between 50 000 and 200 000, an optimum range suitable for shaping the polymers into bags, containers, or other forms that give the adequate protection to food during distribution and storage. The typical properties of common plastic packaging materials are reported in Table 10.1.

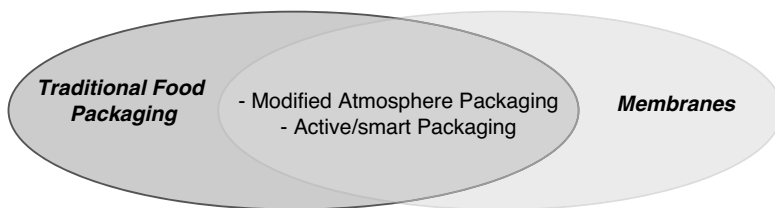
It is important to highlight that the required packaging protection depends on the product characteristics but not always does the proper protection mean the complete isolation of food from the environment-degradation factors. For example, some fatty foods with long shelf life are sensitive to oxygen and light and, as a consequence, the

**Table 10.1** Main properties of plastic packaging materials. (After modification from [1]).

| Material    | Mechanical property      | Moisture barrier | Gas barrier | Use $T$ ( $^{\circ}\text{C}$ ) |
|-------------|--------------------------|------------------|-------------|--------------------------------|
| PE          |                          |                  |             |                                |
| LDPE        | Tough, flexible          | High             | Very low    | -50 to 80                      |
| LLDPE       | Tough, extensible        | High             | Very low    | -30 to 100                     |
| HDPE        | Tough, flexible          | Very high        | Very low    | -40 to 120                     |
| PP          | Moderately stiff, strong | High             | low         | -40 to 120                     |
| PS          |                          |                  |             |                                |
| General     | Stiff, strong, brittle   | Low              | Low         | -20 to 90                      |
| Impact      | Tough, strong            | Low              | Low         | -20 to 90                      |
| PVC         |                          |                  |             |                                |
| Unplastic.  | Stiff, strong            | High             | Moderate    | -2 to 80                       |
| Plasticized | Soft, extensible         | Moderate         | Moderate    | -2 to 80                       |
| PET         | Stiff, strong            | Moderate         | Moderate    | -60 to 200                     |
| PVDC        | Stiff, strong            | Very high        | Very high   | -20 to 130                     |
| EVOH        | Stiff, strong            | Low              | Very high*  | -20 to 150                     |
| EVA         | Tough, extensible        | Moderate         | Low         | -75 to 65                      |
| Nylon       | Strong, tough            | High             | High*       | -2 to 120                      |

ideal preservation requires the absence of oxygen inside the package, so a high barrier material to reduce the oxygen entrance and, possibly, no light transmission through the package has to be used. On the contrary, for minimally processed vegetables, the natural interplay between the respiration of the product and the transfer of gases through the packaging can lead to an appropriate atmosphere within package that contributes to maintaining the product freshness during commercialization. In this specific case, the protection by the packaging is granted by films with proper gas permeability that allow the right exchanges between the internal and external sides of the package and not by high barrier materials. In recent years, besides the traditional basic functions of packaging (i.e. protection, communication, convenience, and containment) extra enhanced functions have been sought by the food-packaging sector to meet the consumer demands for minimally processed foods with fewer preservatives, increased regulatory requirements, market globalization and concern for food safety. Active packaging is the main area in which most of recent innovative ideas have been applied to satisfy these needs, broadening and redefining the function of food packaging [1]. Active packaging has been defined as a system in which the product, the package, and the environment interact in a positive way to extend shelf life or to achieve some characteristics that cannot be obtained otherwise. In other words, active packaging is a new generation of packaging materials that can release active compounds (antimicrobial, antioxidants, enzymes, flavors, nutraceuticals, etc.) or absorb undesirable substances (oxygen, ethylene, moisture, etc.) at controlled rates suitable for enhancing the quality and safety of a wide range of foods during extended storage.

In this context, food packaging and membrane developers started collaborations in order to evaluate how membrane science could be applied to food packaging area. In



**Figure 10.1** Fields of applicability of membranes with respect to traditional food packaging.

fact, the wide range of properties required to the packaging gives the idea to design and synthesize the membranes as devices that should contribute to maintaining food quality. An example is the fact that recently in the International Membrane Conferences held in Korea (ICOM06, Seoul), in USA (ICOM08, Honolulu) and France (ICOM09, Montpellier) a specific session was devoted to food packaging. Moreover, the USA market for nonseparating membranes used in drug delivery, guided tissue regeneration, batteries, food packaging and high-performance textiles was calculated to be \$2.8 billion in 2005, more than half the value of the combined market for all the membranes used in separation and nonseparating applications [2].

The definition of a membrane is not univocal and many attempts have been made to describe it. The most general one may be the following, as reported by Paul and Yampol'skii [3]: "A membrane is a phase or a group of phase that lies between two different phases, which is physically and/or chemically distinctive from both of them and which, due to its properties and the force field applied is able to control the mass transport between these phases."

Membranes, both organic and inorganic, are generally classified based on their morphology as porous, nonporous (dense/tight) and liquid membranes [4]. Depending on the specific membrane properties (porosity, hydrophobicity/hydrophilicity, pore size, etc.), they can be used as packaging materials in modulating the gas-exchange rate between the inside and outside of the package environment (modified-atmosphere packaging) or in actively controlling the release or absorption of specific compounds to or from the packaged food (active packaging). In this chapter, the use of membranes in food packaging will be analyzed under these two main perspectives, giving results of some examples and potential applications. Figure 10.1 shows the fields of applicability of membranes with respect to traditional food packaging.

## 10.2

### Application of Membranes in Controlling Gas Permeability

The transport of gas or vapor through a flexible food package (usually made of polymeric films) can greatly influence the quality of the food and, in many situations, the role of packaging that is in the direction of reducing, as low as possible, the gas exchange between the internal or external side of the package. For example, oxygen

permeability through the package can cause oxidation in lipid foods (dehydrated and processed meat, egg, cheese, fatty foods) that leads to off-flavor production and loss of flavor, color, nutrient value. Water-vapor permeation inside the package can cause moisture gain leading to sogginess or microbial growth in food, while water vapor escaping from the package can cause moisture loss leading to undesirable textural changes in food [1]. The modified atmospheres (MAP) and the under-vacuum packaging for the storage of nonrespiring products, in fact, require the use of high barrier materials able to reduce the loss of gas during storage, to maintain the optimal atmosphere initially flushed. On the contrary, there are occasions when the transport of gases and vapors is desirable. In modified-atmosphere packaging of fresh produce (i.e. respiring products), the exchange of oxygen, carbon dioxide and water vapor through the package is necessary to accommodate the respiration and transpiration of the respiring product and to maintain an optimum gas composition in the package.

As shown in Table 10.1 polymeric plastic materials cover a wide range of permeability performances but, often, it is necessary to combine the characteristics of one or more materials to reach the desired value.

In the field of membranes, gas separation can be considered as a major industrial application of membrane technology thanks to the research achievement in the 1960s and 1970s. This progress refers to the development of membrane structures, which allowed to have high fluxes and large surface area modules [5]. The production of *asymmetric membranes* for reverse osmosis applications by the Loeb–Sourirajan phase-separation process was fundamental for the gas-separation technology growth. Typical asymmetric membranes are made starting from a glassy polymer and the thicknesses of the selective layer are usually between 0.1  $\mu\text{m}$  and 0.5  $\mu\text{m}$ . The main limit of the use of asymmetric dense membranes is that even small defects (pinholes) in the selective membrane, produced during membrane preparation and module manufacture, lead to a decrease of the selectivity of the gas-separation membranes. This problem was partially overcome by coating the membranes with a highly permeable polymer (i.e. silicone rubber), so that the selectivity and flux of the membranes were not significantly affected [5]. A different type of membrane used in gas separation is the *composite membrane*. It is made of a thin selective layer coated on a porous support layer. However, it is difficult to obtain composite membranes with very thin glassy selective layers as those obtained by phase separation. Therefore, composite membranes are usually employed to prepare membranes with a rubber selective layer and the porous substrate to give a mechanical strength.

The gas permeation is a chemical-physical phenomenon that concerns, in food packaging, only permeable packages and in particular those consisting of polymeric parts such as plastic films, rigid plastics containers, plastic-coated papers and metallized plastic films.

Usually, membrane processes that utilize polymers include gas separation (e.g., nitrogen generation from air), vapor permeation (e.g., recovery of volatile organic compounds from gas streams), pervaporation (e.g., dehydration of ethanol) and reverse osmosis (e.g., desalination of water) [6].

Permeation is defined as the movement of gases, vapors or liquids (also called permeant substances or penetrant molecules) across a homogeneous material driven by a concentration gradient in the direction from high to low concentration [1].

The permeation of small molecules through a dense polymeric material is described by a solution diffusion model. In fact, gas molecules on the high-pressure side of the membrane dissolve in the polymer, diffuse down the concentration gradient, and desorb on the low-pressure side of the membrane [7]. The permeability coefficient,  $P$  is the product of a solubility coefficient,  $S$ , and a diffusion coefficient or diffusivity,  $D$ :

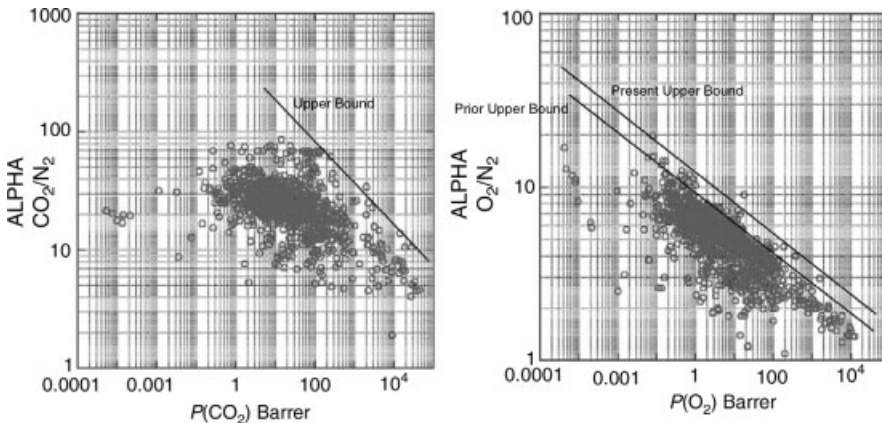
$$P = S \times D \quad (10.1)$$

The permeability coefficient is derived using Fick's first law to model diffusion and Henry's law to model adsorption and desorption [8].

Generally, the measure of the ability of a membrane to separate two gases, A and B, is given by the ratio of their membrane permeability or by the product of the "diffusion selectivity" and the "solubility selectivity" and it is called membrane permselectivity ( $\alpha$ ):

$$\alpha_{A/B} = \frac{P_A}{P_B} = \left( \frac{S_A}{S_B} \right) \left( \frac{D_A}{D_B} \right) \quad (10.2)$$

Most of the recent research in membrane science has focused on developing membrane materials with a better balance of selectivity and permeability as this seems the most likely route for expanding the use of this technology also in food packaging. Figure 10.2 shows the typical trade-off between the  $\text{CO}_2/\text{N}_2$  and  $\text{O}_2/\text{N}_2$  selectivity and  $\text{CO}_2$  and  $\text{O}_2$  permeability, respectively, for a vast number of membrane materials [9].



**Figure 10.2** Upper-bound correlation for  $\text{CO}_2/\text{N}_2$  and  $\text{O}_2/\text{N}_2$  separation. (reprinted from [9], with permission of Elsevier.)

The graph suggests that there exists an inherent relationship between the selectivity of a polymeric material and its permeability. The lines above which no data points exist are called the upper bounds. Over the past 20 years these upper bounds shifted to higher values, however, the direction still remains valid: a high permeable polymer material frequently has a low selectivity and vice versa. Therefore, to overcome such an upper bound motivates material scientists to develop new concepts to realize high productivity as well as high-selectivity membranes. The relationship between the selectivity and polymeric material is of fundamental importance also in designing membranes for specific food packaging application.

### 10.2.1

#### Membranes in Modified-Atmosphere Packaging

The shelf life of horticultural products and minimally processed fruits and vegetables (i.e. fruits and vegetables that have attributes of convenience and fresh-like quality) is limited by respiration, transpiration and enzymatic activity of the living tissue especially after harvest processing and, at the same time, to proliferation of spoilage and pathogenic micro-organisms.

To reduce the effects of these factors it is possible to act on processing or, more usually, on packaging. Modified-atmosphere packaging (MAP) is effective in prolonging shelf life by decreasing  $O_2$  and increasing  $CO_2$  concentrations in the package atmosphere that successively changes as a consequence of respiratory  $O_2$  uptake and  $CO_2$  evolution of packaged product (respiration rate) and gas transfer from the packaged films. In other words, the basic principle of MAP is that a modified atmosphere can be created passively by using properly permeable packaging materials, or actively by using a specified gas mixture together with permeable packaging materials. A proper combination of product characteristics, film permeability and film selectivity results in the evolution of an appropriate atmosphere within packages [10, 11]. The aim is to create an optimal gas balance inside the package, where the respiration activity of a product is as low as possible and on the other hand, the oxygen concentration and carbon dioxide levels are not detrimental to the product. In fact, it has been demonstrated that the respiration rate depends on the concentration of  $O_2$  and  $CO_2$  in which the product is stored after harvesting. Based on these results, several mathematical models have been developed [12, 13]. In particular, the one based on the principles of enzyme kinetics (the Michaelis–Menten kinetic equation) which also take into account the inhibition due to  $CO_2$  is reported here [13]. The suggested form for the rate of  $O_2$  uptake is the following:

$$r_{O_2} = \frac{WR_m p_{O_2}}{k_m + \left[ 1 + \left( \frac{p_{CO_2}}{K_i} \right) \right] p_{O_2}}$$

where,  $p_{O_2}$  and  $p_{CO_2}$  are the partial pressures of  $O_2$  and  $CO_2$ ,  $W$  is the mass of the product, and  $R_m$ ,  $k_m$  and  $K_i$  are the temperature-dependent parameters specific for a particular type of product. A similar equation can be reported also for the rate of  $CO_2$  production,  $r_{CO_2}$ .

The ratio of  $\text{CO}_2$  produced to  $\text{O}_2$  consumed is known as the respiratory quotient, that is,

$$\text{RQ} = \frac{r_{\text{CO}_2}}{r_{\text{O}_2}}$$

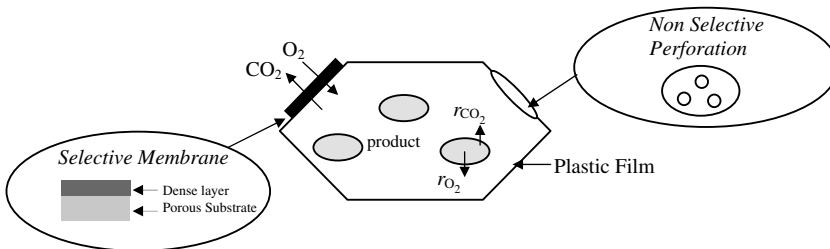
This ratio can range from 0.7 to 1.4 depending on the substrate and metabolic state [14].

Actually, the most difficult task in manufacturing raw ready-to-use or ready-to-eat fruit and vegetable products of good quality and possessing a shelf life of several days is to maintain such optimum concentration of  $\text{O}_2$  and  $\text{CO}_2$ . The main problem is that only a few packaging materials on the market are permeable enough to match with the respiration of fruits and vegetables. Moreover, with fresh respiring products, it would be advantageous for the product shelf life retention to have film permeability increased by temperature, at least as much as the respiration rate increases in order to avoid anaerobic conditions. Unfortunately, the permeation rates of most packaging films are only modestly affected by temperature [15].

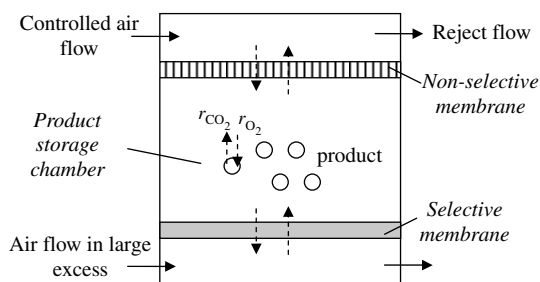
One approach of extending the shelf life of fruits and vegetables by membranes is reported by Paul and Clarke [16]. They worked on modeling the performance of packages containing respiring products that have both a permselective membrane (asymmetric dense membrane, rubber or glassy type) and perforations (nonselective membrane) as shown in Figure 10.3.

Such packaging has the function to regulate the permeation of oxygen and carbon dioxide, respectively into and out of the food packaging, to reach a steady state between the respiring product and the external atmosphere of the packaging. In fact, usually selective membranes are able to create the gas compositions needed only for a certain group of products, since they are too selective in permeation of  $\text{CO}_2$  relative to  $\text{O}_2$ , while perforations are not selective. The model calculations showed that a wide range of gas optimal atmospheres for many fresh products, such as broccoli, mangoes, cauliflower, and so on, can be created using a semi-permeable membrane together with the perforations that provide a nonselective permeation of gases between the air outside the package and the gas mixture inside the package.

In another article, the same authors [17] extended the same concept from small disposable retail packages to reusable large-scale containers for storage and shipping



**Figure 10.3** Schematic drawing plastic food package with a selective membrane patch and nonselective perforations or holes. (After modification from Ref. [16], with permission of Elsevier.)



**Figure 10.4** Scheme of the modified-atmosphere packaging concept of a large-scale, reusable container for storage or shipping of food products combining the use of a selective and nonselective membrane. (After modification from Ref. [17], with permission of Elsevier.)

of food products. The concept is shown in Figure 10.4. Also in this case a selective membrane is used in combination with a nonselective membrane acting in parallel. The relative amount of gas exchange ( $\text{CO}_2$  and  $\text{O}_2$ ) through the nonselective membrane can be adjusted by varying the volumetric air feed rate to its upstream surface that will, in turn, correct the steady-state composition in the product chamber. Therefore, a desired atmosphere can be created by regulating the air feed rate that can reduce the selectivity of the  $\text{CO}_2$  to  $\text{O}_2$  generated by the selective membrane to enable operation at higher  $\text{CO}_2$  concentrations.

Furthermore, the mathematical model developed shows that the lower  $\text{CO}_2$  concentration in the product storage chamber is largely dependent on the selective membrane, whereas, the higher  $\text{CO}_2$  concentration is mostly dependent on the choice of the nonselective membrane. The region between these lower and upper  $\text{CO}_2$  concentration limits required by a wide range of products can be reached by adjusting the air feed rate over a range of 1–2 orders of magnitude.

In another study, Torchia *et al.* [18] reported the application of a novel polymer material, the modified polyaryletheretherketone (PEEKWC), to food packaging. This polymer has excellent chemical, thermal and mechanical properties, and it has the advantage, compared to traditional PEEK, to be soluble in several common organic solvents, facilitating the asymmetric (dense and porous) membrane preparation by phase inversion [19–22].

Different types of membranes with pure PEEKWC and PEEKWC modified with poly- $\alpha$ -pinene (P $\alpha$ P), PEEKWC/P $\alpha$ P, were prepared by solvent evaporation. The films produced, PEEKWC and PEEKWC/P $\alpha$ P, were characterized in terms of gas and vapor transport ( $\text{P}_{\text{O}_2}$  and WVTR) and the results obtained were comparable to those of commercial food-packaging polymers. The potentiality of these materials was tested for MAP of fresh products, such as fruits and vegetables.

The selectivity was calculated as the ratio between the permeability values of the  $\text{O}_2$  and  $\text{CO}_2$  species that obey to the Arrhenius' law in the analyzed temperature range. The activation energy values for the permeation of  $\text{O}_2$  and  $\text{CO}_2$ , respectively, were also calculated. The separation performance,  $\text{CO}_2$  and  $\text{O}_2$  permeability, of the polymer as well as the  $\text{CO}_2/\text{O}_2$  selectivity changed at higher additive concentration as reported in



**Table 10.2** Oxygen and carbon dioxide permeability and activation energy in polymeric films at 5 °C. (After modification from [23]). (Reprinted from [18], with permission of Chirioti Ed.).

| Polymers                | $P_{O_2}$<br>(Barrer) | $P_{CO_2}$<br>(Barrer) | $E_{O_2^p}$<br>(kJ mol <sup>-1</sup> ) | $E_{CO_2^p}$<br>(kJ mol <sup>-1</sup> ) | $\alpha$ (CO <sub>2</sub> /O <sub>2</sub> )<br>(5 °C) |
|-------------------------|-----------------------|------------------------|--|---|---|
| PEEKWC                  | 0.36                  | 2.4                    | 21.7                                   | 11.3                                    | 6.7   |
| PEEKWC/PαP (80/20)      | 0.30                  | 1.7                    | 21.7                                   | 15.3                                    | 5.7   |
| PEEKWC/PαP (50/50)      | 0.12                  | 0.56                   | 37.4                                   | 31.3                                    | 4.7   |
| Silicon rubber          | 100                   | 65                     | 8.4                                    | —                                       | 6.5   |
| Natural rubber          | 8.7                   | 61.4                   | 31.4                                   | 25.5                                    | 7.1   |
| Polybutadiene           | 7.7                   | 71                     | 29.7                                   | 21.8                                    | 9.2   |
| Poly(butadiene-styrene) | 6.7                   | 59.6                   | 30.5                                   | 23.8                                    | 9.2   |
| LDPE                    | 1                     | 7.4                    | 43.1                                   | 34.2                                    | 6.7   |
| HDPE                    | 0.014                 | 0.07                   | 35.1                                   | 30.1                                    | 4.8   |
| PA 6                    | 0.007                 | 0.035                  | 43.5                                   | 40.6                                    | 4.7   |
| Saran                   | 0.0004                | 0.0042                 | 66.5                                   | 51.5                                    | 10.2  |
| PET                     | 0.013                 | 0.045                  | 26.8                                   | 25.9                                    | 3.4   |
| Cellulose acetate       | 0.34                  | 2.9                    | 20.9                                   | 29.7                                    | 8   |
| PVC                     | 2.1                   | 12.7                   | 36.9                                   | 27.6                                    | 6.1   |

Barrer = 10<sup>-10</sup> (cm<sup>3</sup> (STP) cm/cm<sup>2</sup> s cmHg).

Table 10.2. The CO<sub>2</sub>/O<sub>2</sub> selectivity, measured through the PEEKWC films, is comparable to that of LDPE and silicone rubber films. The O<sub>2</sub> permeability is about one third higher than LDPE but two orders of magnitude lower than silicone rubber. PEEKWC/PαP 50/50 films were characterized by a CO<sub>2</sub>/O<sub>2</sub> selectivity of 4.7 similar to the one of HDPE and Nylon 6. In this case, the O<sub>2</sub> permeability of PEEKWC/PαP 50/50 results 8.5 and 170 times, respectively, higher than that measured in the previous commercial polymers. Oxygen and carbon dioxide permeability of PEEKWC were similar to cellulose acetate ones

In Table 10.3, an increase of the activation energy for CO<sub>2</sub> permeation is also observed when the additive amount rises. On the other hand, the activation energy, calculated for oxygen, is constant up to 20% PαP concentration, it increases significantly at 30% of additive, remaining almost constant up to 50/50 PEEKWC/PαP ratio. The CO<sub>2</sub>/O<sub>2</sub> selectivity, calculated for pure and added PEEKWC films, suggests its use in food packaging only for a restrict number of fresh products packaging, see Table 10.3 [18].

Concerning the permeability of PEEKWC films, with and without additive, it is still too low with respect to the majority of fresh fruit and vegetables studied. However, this limitation can be extended generally to all polymeric materials. Only a few packaging materials on the market are permeable enough to match with the respiration of fruit and vegetables. Most films do not result in optimal O<sub>2</sub> and CO<sub>2</sub> atmospheres, especially when the product has a high respiration rate. Therefore, the development of novel membranes, that is, loaded with nanostructure material, or, alternatively the presence of nonselective membranes, as previously discussed [16], carefully distributed in the packaging, could extend the use of PEEKWC or other polymeric material to a broader number of products.

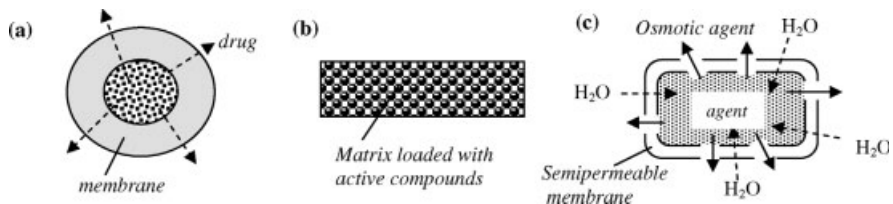
**Table 10.3** Oxygen and carbon dioxide permeability ( $P^R_{O_2}$  and  $P^R_{CO_2}$ ) and selectivity ( $\alpha^R$ ) required for various fruits and vegetables in typical market size packages [23] compared with PEEKWC based films. Film thickness 25 mm and 4 °C. (Reprinted from [18], with permission of Chiriotti Ed.).

| Fresh products    | $P^R_{O_2}$ | $P^R_{CO_2}$ | $\alpha^R$ ( $CO_2/O_2$ ) | $\alpha$ ( $CO_2/O_2$ ) of PEEKWC films   |
|-------------------|-------------|--------------|---------------------------|---|
| Strawberry        | 22.4        | 23.9         | 1.1                       |   |
| Bruxelles sprouts | 12.7        | 76.6         | 6                         | (90/10) and (80/20)<br>PEEKWC/P $\alpha$ P ( $\alpha = 5.7$ ),<br>PEEKWC ( $\alpha = 6.7$ ) |
| Mushrooms         | 10.6        | 13.1         | 1.3                       |   |
| Lettuce           | 4.5         | 42.94        | 9.5                       |   |
| Turnip            | 2.2         | 7.6          | 3.5                       | (70/30) PEEKWC/P $\alpha$ P<br>( $\alpha = 4$ )   |
| Carrot            | 1.54        | 5.7          | 3.7                       | (70/30) PEEKWC/P $\alpha$ P<br>( $\alpha = 4$ )   |
| Apple             | 1.51        | 9.5          | 6.3                       | (90/10) and (80/20)<br>PEEKWC/P $\alpha$ P ( $\alpha = 5.7$ ),<br>PEEKWC ( $\alpha = 6.7$ ) |
| Celery            | 1.26        | 4.04         | 3.2                       |   |
| Green Pepper      | 0.67        | 4.03         | 6                         | (90/10) and (80/20)<br>PEEKWC/P $\alpha$ P ( $\alpha = 5.7$ ),<br>PEEKWC ( $\alpha = 6.7$ ) |
| Tomato            | 3.65        | 19.2         | 5.3                       |   |
| Blackberry        | 6.4         | 20.1         | 3.14                      |   |

Barrer =  $10^{-10}$  (cm<sup>3</sup> (STP) cm/cm<sup>2</sup> s cmHg).

### 10.3 Membranes as Devices for Active Food Packaging

The concept of controlled delivery using membranes has been mainly applied in the medical field in which a membrane is used to moderate the rate of delivery of drug to the body. The application of the membrane differs depending on the type of device employed [24], as shown in Figure 10.5: (a) the membrane has the function to control the permeation of the drug from a reservoir to achieve the desired drug-delivery rate (*reservoir system*); (b) the drug is dispersed or impregnated into the membrane material and it slowly dissolves or degrades in the body. In this case, the drug



**Figure 10.5** Illustration of the membrane controlled-release devices: (a) reservoir system; (b) matrix system, (c) osmotic system.

delivery is controlled by a combination of diffusion and biodegradation (*matrix system*); (c) the drug is released using the osmotic pressure developed by diffusion of water across a semipermeable membrane into a salt solution that pushes it out (*osmotic system*).

These concepts have also been extended to other areas of interest to control the delivery of agrochemicals (pesticides), household products (fragrances) and active agents for food-packaging applications (antimicrobials, antioxidants, aroma compounds).

Active packaging has been defined as a system in which the product, the package, and the environment interact in a positive way to extend shelf life or to achieve some characteristics [25]. A new challenge in the food industry is the current trend in consumer demands for minimally processed, easily prepared and ready-to-eat fresh products. Traditional preservation of such products, in which the preservative is added directly to the food, has limited benefits. In fact, the active substances are neutralized on contact or diffuse rapidly from the surface, where contamination primarily occurs, into the food mass [26]. Moreover, the addition of large amounts of antimicrobials directly to ready-to-eat products can influence the taste, while low amounts result in a short shelf life. The controlled release of agents obtained by an active food-packaging system can be generally considered the solution to preserve the quality and increase the storage time for ready-to-eat perishable foods [27]. All the active packaging technologies involve some physical, chemical, or biological action for generating interactions between the package, the product, and the package headspace to increase the shelf life of foods. In addition, they can be divided into categories of absorber, releasing system and other systems [26]. The actual techniques can be summarized as follows:

- addition of sachets/pads containing volatile agents;
- incorporation of volatile and nonvolatile agents directly into the polymers;
- coating or absorbing agents onto polymer surfaces;
- immobilization of agents to polymers by ion- or covalent linkages;
- use of polymers that are inherently antimicrobial;
- multilayer films with active layer.

In particular, multilayer films are an interesting solution for active packaging and membranes could have a key role in these multilayer structures. In monolayer dense film in fact only a part of the preservative is released [28, 29] and higher concentrations of antimicrobial agents than usually needed have to be loaded in these films to preserve the food. Moreover, the release rate of the active compounds is not easily controlled.

The multilayer films presented in the literature are usually produced by coextrusion of dense film or coating of an active thin layer on the polymer surface; the active layer functions both as reservoir and as release control of the active substance [30–32]. In the literature, only few works report the preparation of multilayer films, having an outer barrier dense layer, an active agent-containing matrix layer and a release-control layer. The control layer is the key layer to control the initial time-lag period and the flux of penetration of the active agents. In these multilayer structures the membranes

are suitable devices. Han *et al.* [33], for example, suggested the use of such multilayer structure for antimicrobial-release packaging systems. Another study on multilayer films concerns the controlled release of a volatile antimicrobial compound, the allylthiocyanate (A.I.T.C). The multilayer film is made of (a) a tie-layer, cyclodextrins containing the A.I.T.C and (b) perforated membrane, within a fine powder of silica gel, which is in contact with the food product [34].

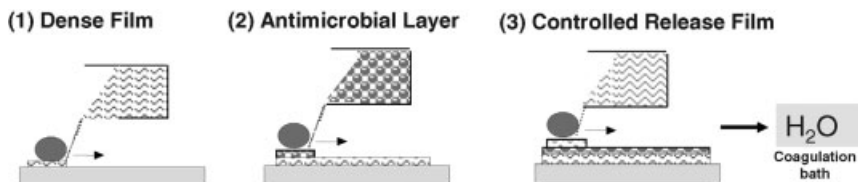
Figoli *et al.* introduced the use of the asymmetric porous membrane in controlled-release food packaging, produced by nonsolvent-induced phase separation (NIPS) technique [35, 36]. They reported the development of an antimicrobial food packaging film based on the use of membranes, with modulate porosity, as a controlling release system. The multilayer film was made of three layers: an outer dense layer to control the exchange rate of gases between the external and internal environment of the food packaging, an intermediate adhesive tie-layer which has also the function of reservoir of antimicrobials, and the porous membrane layer, made by phase inversion, that controls the release of antimicrobials to the food. In particular, its properties (porosity and morphology) can be properly tailored by changing the phase-inversion process conditions.

In this case, the investigated polymer was the modified polyaryletheretherketone (PEEK-WC), already widely used in membrane preparation [20, 22]. However, the proposed process can be extended also to other polymer traditionally employed in food packaging.

The multilayer films were prepared as shown in Figure 10.6. All separate layers of the multilayer film could be cast subsequently on one another without removing the dense film from the glass substrate.

The method to produce the three layers is presented, as follows:

- 1) The dense PEEK-WC/poly- $\alpha$ -pinene (p- $\alpha$ -p) (different ratio, from 100/0 to 50/50) layer, used as substrate for the multilayer film, was prepared by casting solution. A dense PEEK-WC/p- $\alpha$ -p film was formed on the clean glass substrate after the solvent was evaporated. The addition of p- $\alpha$ -p has the double function to increase the affinity of the dense film with the second layer and to modify the transport properties of the film itself.
- 2) The second layer was made of p- $\alpha$ -p with and without oxalic acid (0.5, 10 and 25 wt%). The starting solution was stirred and cast at 0% RH and 70 °C in a climate chamber. Immediately after casting, the formed double layer film was removed from the climate chamber and allowed to cool at room temperature.

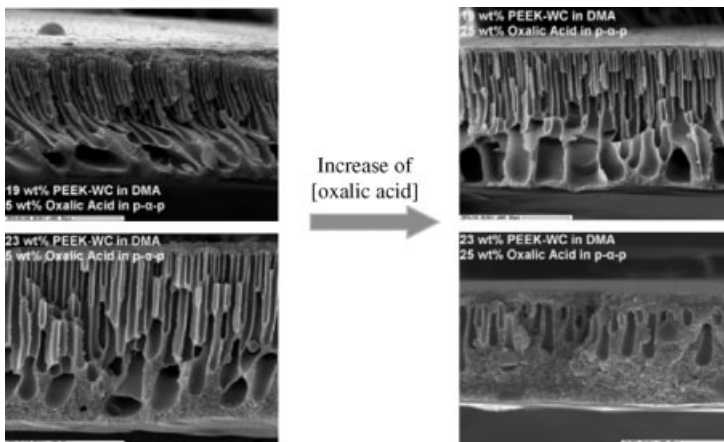


**Figure 10.6** Schematic representation of the multilayer film casting process developed.

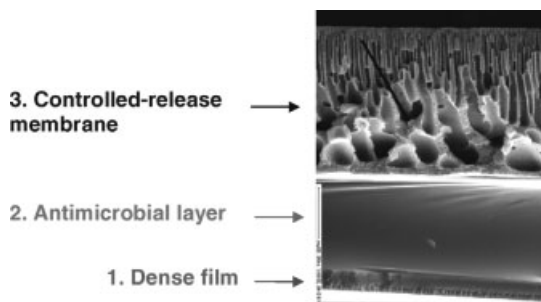
- 3) A porous PEEK-WC film was then cast on the double-layer film previously prepared. The porous membrane layer was prepared by dry-wet phase inversion. A casting solution was produced with different concentrations of PEEK-WC in *N,N* diethylacetamide (DMA) (15, 19 and 23 wt%). The films were cast in a climate chamber at 50% RH and 20 °C. The porosity and morphology of each membrane were varied changing the time of exposure to air before precipitation (45 s/240 s.) and the water-bath temperature (0 °C and 40 °C). The multilayer film was removed 5 min after immersion from the coagulation bath. The same PEEKWC membranes have also been prepared by casting the solution directly on the glass substrate to evaluate the effect of the poly- $\alpha$ -pinene substrate, with and without oxalic acid, on the properties (i.e. morphology, porosity) of the membrane. The different membranes obtained by varying the concentration of oxalic acid and polymer, are illustrated in Figure 10.7. In particular, the increase of the polymer concentration (from 19 to 23 wt%) produces an asymmetric dense membrane.

The final antimicrobial multilayer films have also been examined by scanning electron microscopy, SEM. The individual layers of the film, indicated by the arrows, can clearly be distinguished in the picture (Figure 10.8).

The release rates of oxalic acid from the multilayer film was determined by bringing into contact the porous membrane side with distilled water and monitoring the change of pH with time. The results proved that the release rate depended strongly on the phase inversion processing conditions and on the compounds used in the preparation of porous membrane layer (air exposure time, water-bath temperature, polymer concentration, oxalic acid concentration). In particular, the oxalic acid release increased with decreasing the coagulation bath temperature (from 40 to 0 °C) and when the operating temperature was increased from 5 to 25 °C [35, 36].



**Figure 10.7** SEM cross-sections of the different membranes (release layer) obtained by changing the concentration of oxalic acid (from 5 to 25 wt.%) and PEEKWC polymer (from 19 to 25 wt.%).



**Figure 10.8** Cross-section of the multilayer film (SEM magnification of 400 $\times$ ).

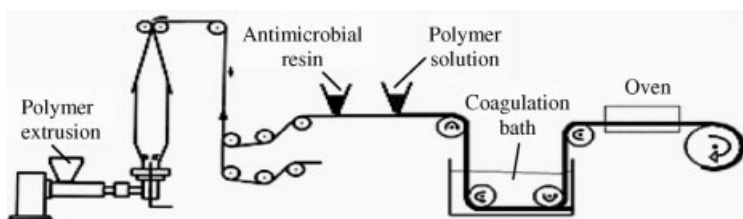
Based on these results, a production line for scale production of the multilayer film was proposed as shown in Figure 10.9.

The polymer is extruded to produce a dense film with barrier or specific gas or water-vapor properties, then, a commercial tie-layer resin, loaded with a specific antimicrobial, is cast on the dense film. Finally, the polymer solution is spread on the adhesive layer and brought into contact with the coagulation bath (i.e. water) that will determine the formation of the asymmetric porous membrane.

Another example reported in the literature is that of Altinkaya *et al.* who presented the incorporation of lysozyme [37] and natural antioxidants [38], such as L-ascorbic acid and L-tyrosine, into cellulose acetate (CA) asymmetric porous structures by phase-inversion technique. In order to achieve controlled release of the active compounds studied, the films structure was modified by changing the morphology (from porous to dense) tailoring the composition of the initial casting solution.

In particular, the films were produced using the dry phase-inversion technique. The polymer was dissolved in a mixture of acetone and water and, then, cast on a support and exposed to an air stream. Different morphologies were obtained by changing the phase-inversion processing conditions such as evaporation temperature, relative humidity, wet casting thickness as well as the composition of the membrane-forming solution.

In the case of lysozyme [37], the highest release rate and antimicrobial activity were obtained with the film prepared with 5% CA solution including 1.5%



**Figure 10.9** Production line suggested for the fabrication of the multilayer film with the asymmetric membrane as the antimicrobial controlled-release system.

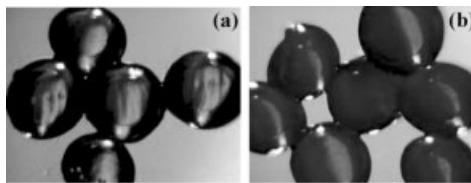
lysozyme. At higher CA concentration (15%) the porosity of the film was reduced with a consequent decrease of the release rate. The diffusion of lysozyme in CA, porous and dense, films was  $4.17 \times 10^{-10} \text{ (cm}^2 \text{ s}^{-1}\text{)}$  and  $1.50 \times 10^{-10} \text{ (cm}^2 \text{ s}^{-1}\text{)}$ , respectively.

The mechanical properties of the films were evaluated also in terms of tensile strength, % elongation at break and Young's modulus. The tensile strength, Young's modulus and elongation at break of the films increased with increasing CA concentration due to reduced pore sizes and porosity of the films.

The incorporation of lysozyme into the films prepared with 5% and 10% CA solution did not determine any change in the mechanical properties with respect to the films without lysozyme. In contrast, the film prepared with 15% of CA loaded with lysozyme showed a significant reduction in tensile strength and elongation at break values. Also, in the case of the loading of low molecular weight natural antioxidants [38], such as L-ascorbic acid and L-tyrosine, the diffusion rate through the films was reduced by increasing the CA concentration in the casting solution. The use of the porous or dense structure in contact with food environment and the different CA concentration of the made film are the main factors responsible of the release rate of these active compounds. The diffusion rate of L-ascorbic acid was  $3.33 \times 10^{-10} \text{ (cm}^2 \text{ s}^{-1}\text{)}$  and  $1.67 \times 10^{-10} \text{ (cm}^2 \text{ s}^{-1}\text{)}$  in porous and dense structures, respectively, while for L-tyrosine was  $1.00 \times 10^{-10} \text{ (cm}^2 \text{ s}^{-1}\text{)}$  and  $0.8 \times 10^{-10} \text{ (cm}^2 \text{ s}^{-1}\text{)}$  in porous and dense structures, respectively. Also the mechanical properties of the films increased significantly on increasing the CA concentration, due to the fact that the films produced had a lower porosity, pore size and they were practically dense.

Figoli *et al.* [39], recently illustrated the advantages of using microencapsulation as a promising technology for protecting the natural active substances from the stresses and damages that can occur during food-package manufacturing and for improving the active-agent distribution. Thanks to these effects and according to their structure, the microcapsules could better control the release of the active substances and promote the interaction of the film with the active substances carrier. In this work, bio-microcapsules of chitosan have been developed using a system that combines the membrane process concept with the phase-inversion technique using a monoporous polymeric film [40]. This technique permitted the formation of monodispersed biopolymer droplets that were then cross-linked with a natural additive adapted for this polymer structure, and that enhanced the water resistance of chitosan itself. The capsule size and morphology were adjusted by changing the ingredient parameters such as the cross-linking concentration and tailored with the pore diameter of the monoporous film employed. Furthermore, two different types of natural antimicrobial were included in the capsules enabling loading both during their production and after the droplet formation. The chemical-physical analysis of the new chitosan microcapsules was carried out by means of optical microscopy, SEM and EDX. The chitosan capsules produced are shown in Figure 10.10.

The antimicrobial activity of the microcapsules was assayed by turbidimetric methods against *Staphylococcus aureus* selected as a pathogen micro-organism, which



**Figure 10.10** Optical microscope image of chitosan microcapsules without (a) and with (b) antimicrobial compound.

may be present in fresh food. The results showed that the addition of the antimicrobials enhanced the antimicrobial effect of chitosan itself and the growth of *Staphylococcus Aureus* was totally inhibited.

#### 10.4

#### Conclusion

In a period in which consumers are demanding higher-quality foods and changes in retailing practices (such as market globalization resulting in longer distribution of food), or the consumer's way of life (resulting in less time spent shopping for fresh food at the market and cooking), the major challenge to the food-packaging industry is the development of new packaging concepts that extend shelf life while maintaining and monitoring food safety and quality. In this context, membranes can play an important role and, even if their potentialities have not been completely exploited, some promising membrane features in food packaging have been reported and discussed in this chapter. Their use has been addressed toward two main perspectives: (a) modulating the gas exchange rate between the inside and outside of the package environment (such as some applications of modified-atmosphere packaging) and (b) actively controlling the release or absorption of specific compounds from the packaged food (active packaging). In particular, the possibility of tailoring the membrane morphology, porosity and properties allows an extension of their use to a broad range of food-packaging purposes.

Furthermore, the growing environmental awareness coupled with the inexorable rise of pre-packaged disposable meals has directed the research to the development of environmentally friendly packaging materials with biodegradable properties, preferably with components from natural sources rather than from petrochemical materials. Even if up to now biopolymers have been slow to reach commercial maturity, due to their high costs and less optimal physical properties than conventional plastics, things are changing, and new large-scale production systems are bringing down the costs of biodegradable polymers, and sophisticated polymerization and blending techniques are improving the material properties.

In this continuously evolving scenario, the design and production of innovative packaging is of fundamental importance and membranes can have a key role and actively contribute to this innovation.



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