Lipids and Biopackaging

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ABSTRACT: Packaging is important to preserve food quality. It is a barrier to water vapor, gas, aroma, and solute migration between the food and the environment. With the recent increase in ecological consciousness, research has turned toward finding biodegradable materials. The different kinds of biopackaging are discussed with special focus on edible films. The aim of this review is to focus on the influence of lipids used in edible films, mainly for their efficiency as water-vapor barriers. The structure, degree of saturation, chainlength, physical state, shape and dimension of crystals, and distribution of lipids into the film influence the functional properties of the film. In general, the performance of edible films is lower than that of synthetic films, but their main advantage is to be easily, fully, and rapidly biodegradable.

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In food conservation, organoleptic and nutritional characteristics depend mainly on the packaging and its barrier properties against the outer environment; they are able to ensure effective protection against many kinds of degradation. In the last 20 years, petrochemical polymers, commonly called "plastics," have been the most widely used polymers for packaging because of their high performance and low cost. However, plastic materials also present the serious problem of environmental pollution. Environmental policies, such as recycling or incineration, which are alternatives to classic elimination, still pose some technical and logistic problems. A valid solution has been found with the use of biodegradable materials, made from natural fibers or substances, which are called biopolymers and are presented later.

Another problem in the use of plastic for food packaging is that polymeric materials generally are not completely inert. Transfer of substances from the plastic packaging (additives, plasticizers, monomers, by-products from polymer degradation, solvent residues from polymerization, etc.) to the foods with which they come in contact can occur. Toxicological risks and off-flavors are then the result (1). A transfer of some substances from food to packaging can also occur. The composition of the packed food (e.g., fat content, pH, dry matter and aroma compounds, which are organic molecules) may influence the characteristics of the packaging material. Fat especially, migrating into plastics like polyethylene or polypropylene, increases the mobility of plastic film ingredients. This may increase the migration of plastic molecules into the packed food (2) and may change the properties of the packaging material, e.g., decrease the mechanical and/or barrier resistance or even induce stress cracking (3). The migration of molecules from packaging to food tends to increase with fat or alcohol content in the food (4,5). In most situations, this is due to the higher solubility of the migrating organic compounds in fat, compared to water, and is not caused by an increase in the diffusion coefficient owing to interactions between the fat and plastic, as is often assumed (6).

From these observations then arises both the need to find biodegradable packaging polymers to solve the problem of pollution and the need to make edible polymers with food-grade additives to prevent unwanted migrations.

Three kinds of biodegradable films exist (7): (i) *Synthetic polymer/biopolymer mixture*s. These are films made from extrusion mixing of granular native starch (5–20%) and prooxidative and autooxidative additives with synthetic polymers. Their biodegradability is highly controversial (8) and is limited to "biofragmentation" into small particules. It is possible to add more starch (45–75%) if it is pregelatinized, but additional substances are needed that have hydrophobic interactions with the synthetic polymer and hydrophilic interactions with starch. (ii) *Microbial polymers.* These are produced by fermentation of agricultural substrates; they are films made from polyhydroxybutyrate (PHB) or polyhydroxyvalerate (PHV) and polylactic or polyglycolic acids, obtained from biotechnologies. They are totally recyclable and biodegradable, but their applications are currently limited by the prohibitive high price. (iii) *Agricultural polymers*. They are used directly as basic packaging materials and are made from polymers of agricultural origin (e.g., whole grains, flours, proteins, starches). The most developed are "all-starch" packagings made from thermoplastic starches; their applications are limited because of their sensibility to water, but an improvement of water resistance and mechanical properties can be obtained with chemical modifications of

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the polymer: Thiebaud and Borredon (9) obtained thermoplastic and hydrophobic films by esterification of lignocellulosic materials from wood. Relatively insoluble and resistant films can be obtained by crosslinking cotton proteins in a film-forming solution by addition of formaldehyde, glutaraldehyde, etc. (10). Packagings made with such substances have the advantage of being completely biodegradable and also edible when food-grade additives are used (edible coatings or films). Moreover, they are economical because of the low cost of raw materials and are promising in creating new markets for agricultural products. The disadvantage is that, usually, as biodegradability increases, the mechanical and barrier performances decrease (11).

The aim of this review is to focus on the importance of lipids in biopackaging and in particular in edible films. Because of their hydrophobic character, they are moisture transfer barriers. Microbiological and physicochemical degradation is thus prevented by them. Their efficiency in this aim depends on the nature of the lipid used, and in particular on its structure, chemical arrangement, hydrophobicity, physical state (solid or liquid), and on lipid interactions with the other components of the film, such as proteins and polysaccharides.

First, to better understand the behavior and then the influence of lipids in edible films, their interactions with other constituents of edible films and food (water, proteins, and polysaccharides) are discussed. The influence of temperature is also considered.

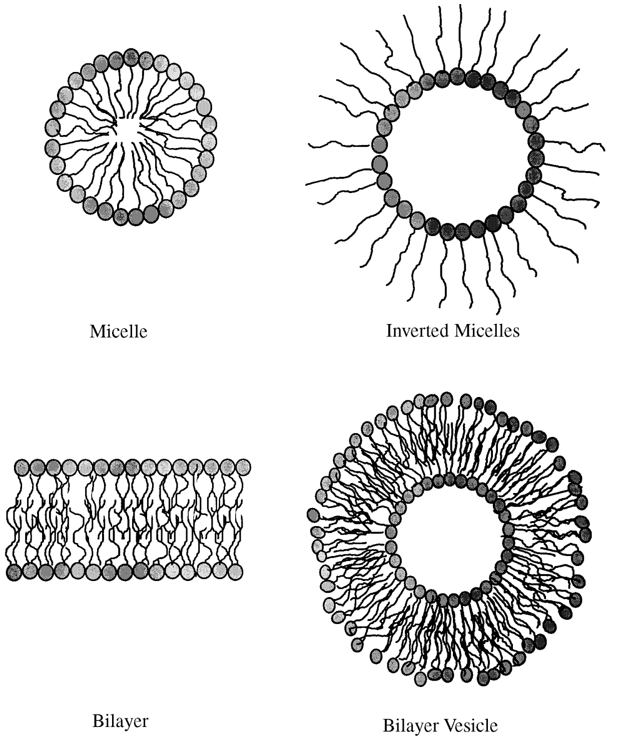

FIG.1. Examples of organized structures formed by lipids in the presence of water.

Lipid–water interactions. In water, lipid molecules have a remarkable behavior: they form micelles, monolayers, bilayers, membranes or vesicles (Fig. 1), not because of exceptionally strong attractive forces but because water has such a strong cohesive self-attraction that it repels the hydrocarbon chains (hydrophobic effect) (12). Variations of polarity can

TABLE 1
Classification of Biologically Active Lipids[a]

Class	Surface properties	Bulk properties	Examples
Nonpolar	Not spread to form monolayer	Insoluble	Paraffin oil; waxes with long-chain fatty acids
Polar			
Class I: insoluble, nonswelling amphiphiles	Spread to form stable monolayer	Insoluble or solubility very low	Tri-, diglycerides; cholesterol; vitamins A, D, E, K
Class II: insoluble, nonswelling amphiphiles	Spread to form stable monolayer	Insoluble but swell in water to form lyotropic liquid crystals	Phospholipids; monoglycerides
Class IIIA: soluble amphiphiles with lyotropic mesomorphism	Spread but form unstable monolayer owing to solubility in aqueous substrate	Soluble, form micelles above a critical micellar concentration; at low water concentrations, form liquid crystals	Detergents; lysolecithin; salts of long-chain fatty acids; gangliosides
Class IIIB: soluble amphiphiles, no lyotropic mesomorphism	Spread but form unstable monolayer due to solubility in aqueous substrate	Form micelles but not liquid crystals	Bile salts; rosin soaps; saponins

[a]Adapted from Small (Ref. 13).

explain the different efficiencies of lipids as water-vapor barriers in edible films. Small (13) has classified lipids according to their polarity (Table 1).

Waxes belong to the nonpolar lipid class; they are insoluble in bulk water and do not spread to form a monolayer on the surface. Their hydrophobicity is high, and this is proven by their solubility in typical organic solvents, such as hexane, chloroform, or benzene. These molecules either have no polar constituents (pure hydrocarbons) or possess a hydrophilic part so small or so buried in the molecule that it cannot readily interact with water, thereby preventing the molecule from spreading. That explains why, in edible films, waxes are the most efficient lipid barriers to water-vapor transfer. Waxes are often used in emulsion for coating fruits and vegetables (14–17).

Triglycerides belong to class I of polar lipids. They are insoluble in bulk water but will spread at the interface to form a stable monolayer. Triglycerides' water affinity, or hydrophobicity, depends upon their structure. Long-chain triglycerides are insoluble in water, whereas short-chain molecules (e.g., triacetin, tributyrin) are partially water soluble. Above a given concentration, they form aggregates similar to micelles. To the same class belong the fatty acids and fatty alcohols with long chains. Palmitic acid, stearic acid, lauric acid, and stearyl alcohol, for instance, present efficient moisture-barrier properties when used in edible films. Kamper and Fennema (18) prevented water migration from tomato paste to crackers with a bilayer film of palmitic–stearic acid and hydroxypropylmethylcellulose.

Monoglycerides belong to class II or III, depending on their chainlength. Concerning class II, lipids are insoluble in water, but water is soluble in the hydrophilic part of their structure, causing them to swell. In the absence of water, they are sparingly soluble in typical organic solvents; in the presence of water, they are quite insoluble in organic solvents and tend to go to the aqueous–organic interface. Thus, they are good emulsifiers. Interesting structures result from the interaction of water with monoglycerides. At low water concentration, they form inverted micelles, with the polar heads toward the inside (molecules with larger hydrophobic parts and smaller or less charged polar heads); at higher water concentrations, micelles are of the normal type with polar groups protruding into the aqueous phase (Fig. 1).

Monoglycerides are used in edible films as emulsifiers, especially for stabilizing emulsified film (19), but also for increasing adhesion between two parts with different hydrophobicity (between the film and the food or between the lipidic layer and the hydrocolloid layer in a bilayer film). Acetylated monoglycerides are often used in edible film formulations to coat frozen food because of their plasticizer characteristics (14,20).

Lipid–protein and lipid–polysaccharide interactions. Because of their amphiphilic character, polar lipid and protein interactions result from a subtle balance between forces of different nature, mainly electrostatic and hydrophobic. For instance, Le Meste and Davidou (21) reported that the interactions between lipid and gluten result from lipid polar head–gliadine electrostatic interactions and from lipid hydrocarbon chain–glutenin hydrophobic interactions. Gontard *et al.* (22) reported that the effects of lipids on the functional properties of gluten-based composite films depended on the interactions between the lipids and the protein structural matrix: beeswax films were opaque and weak, while diacetyl tartaric ester of monoglyceride films stayed transparent and increased their mechanical properties.

The affinity of a lipid for a protein depends greatly upon whether the lipid molecule is isolated or included into a monolayer, as well as upon numerous other parameters, such as the structure and polarity of both lipids and proteins, the molecular lipid/protein ratio, and the environmental conditions (pH, polarity, ionic strength, viscosity, temperature, etc.).

Interactions of lipids with proteins in foodstuffs largely relate to the behavior of these components when together at interfaces and the resulting effects on stability and texture of dispersed systems, such as emulsions and foams (23). The study of the behavior between lipids, proteins, and polysaccharides in the dispersed system can help to comprehend the functional properties of emulsion-based edible films. For example, destabilization of a film-forming emulsion gives emulsified films with poor mechanical and barrier properties (19). Droplets in a stable emulsion are prevented from flocculating either by electrostatic stabilization and steric stabilization or by a combination of the two. Proteins and lipids can ensure electrostatic stabilization because they can form a charged interfacial film (Fig. 2). The composition of interfacial films depends on the ability of the different molecules to adsorb and to anchor at the interface. Krog (24) reported that the stability of protein-based emulsions increases when a low concentration (c) of emulsifier is present ($c < 0.03\%$), whereas the stability decreases as the emulsifier concentration increases ($c = 0.3\%$) owing to desorption of interfacial proteins. At the interface, lipid–protein interactions often result in a preferential clustering of specific lipids around the protein, the favored lipids being those that can be packed most easily around the protein or specifically interact with it (21).

While proteins and lipids stabilize the dispersed systems on account of an electrostatic effect, polysaccharides are usually used because of their ability to stabilize an emulsion by steric effects (Fig. 2). That is why they are called "stabilizers." The essence of a good steric stabilizer is that it should be strongly attached to the surface, but it also should protrude significantly into the continuous phase to form a polymeric layer or a network of appreciable thickness. An example is arabic gum; it is composed of many fractions, but the one that carries the emulsifying ability is an arabinogalactan–protein complex fraction. It is believed that such molecules behave much like graft copolymers with the hydrophobic amino acid residues, anchoring them to the interface oil/water with the hydrophilic carbohydrated blocks extending out into solution, preventing droplet flocculation and coalescence because of steric repulsive forces (25) (Fig. 3). In the formulation of edible films polysaccharides are generally used for their ability

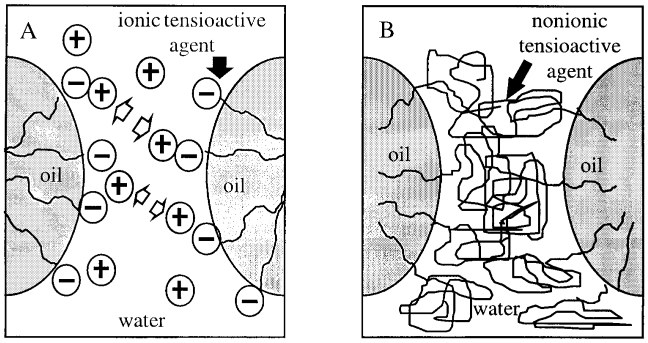

FIG. 2. Representation of interface water–oil: (A) electronic repulsion; (B) steric repulsion.

to form a continuous network, responsible for the mechanical properties of the film.

Influence of temperature. Study of the influence of temperature on the behavior of lipids and polymers is needed to understand the different performances observed between edible films prepared and stored at different temperatures. Changes in temperature cause changes in the physical state of lipids. Decreasing the temperature may induce changes in the physical state of the lipid/water interface, such as transition from a liquid crystal to a gel phase. Le Meste and Davidou (21) reported that, at low temperature, crystallization of phospholipids induces exclusion of the protein molecules from the crystal lattice.

Also, temperature influences solubility. Some molecules may be quite insoluble at low temperature, but on passing to a higher temperature, they undergo chain melting, which allows water to penetrate to the hydrophilic region, thereby permitting the formation of liquid crystals or micelles. The transition temperature from a tightly packed crystal (lamellar and cubic), or even the relatively loosely packed hexagonal chain state, to a more liquid state determines the physical characteristics of the lipid. The physical state of lipids and the shape and orientation of their crystals influence the moisture-barrier efficiency of edible films (26,27).

Temperature influences the surface tension of most liquids (water, oils, and fatty acids); it decreases when the temperature increases. At the critical temperature, the value of surface tension is near zero, so that less energy is needed to form new interfacial surfaces and small globules of dispersed phase are easily obtained.

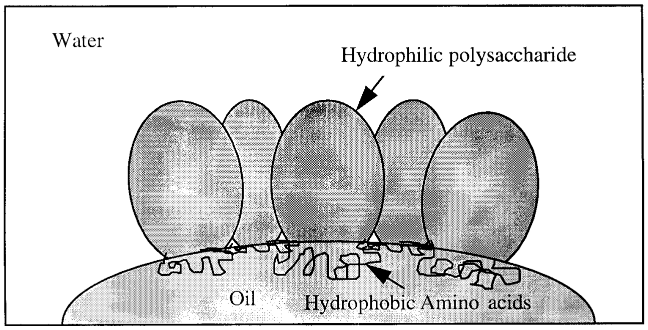

FIG. 3. Schematic illustration of the structure of arabinogalactan–protein complex at the oil–water interface. Adapted from Phillips and Williams (Reference 25).

Additionally, temperature influences the structure of proteins; an increase may induce denaturation of the protein structure. Temperature improves the protein's emulsifying performance by increasing macromolecular flexibility and better exposing its hydrophobic side-chains. Binding a protein with fatty acids stabilizes it against heat denaturation (28).

Moreover, temperature influences viscosity. A decrease of viscosity in an emulsion can decrease its thermodynamic stability. Debeaufort and Voilley (19) reported that an increase of the drying temperature of emulsified edible films can influence the gelatinization of methylcellulose and then the structure of the network.

The properties of lipids and their interactions with proteins and polysaccharides can be extrapolated to better understand and improve biopackaging performances. A review concerning the influence of lipids, specially in edible films, follows.

LIPIDS IN EDIBLE FILMS

A packaging film must generally be resistant to breakage and abrasion (to protect the food and for ease handling) and flexible (enough plasticity to adapt to possible deformation of the filling without breaking) (7). Furthermore, it must be a barrier against water-vapor and oxygen transfer, which are the main factors responsible for organoleptic degradation, physicochemical modification, loss of texture, and microbiological spoilage of the food during preservation.

Generally, films composed of one substance have either good barrier or good mechanical properties but not both. Indeed, the desirable properties of different materials are combined to form composite films: polysaccharides and proteins establish polymer interactions and create a network responsible for the mechanical properties, but they are not efficient water-vapor barriers because of their hydrophilic nature; on the contrary, lipids provide for the film their water-vapor barrier property because of their hydrophobic character, but films made from lipids alone are usually too brittle (14,29). In Tables 2–4, some values of water-vapor permeabilities of some edible and plastic films are reported. The lipids most used are fatty acids with a number of carbon atoms between 14 and 18, mono-, di- and tristearin, stearyl alcohol, hydrogenated and nonhydrogenated vegetable oils, and waxes (beeswax, candelilla, paraffin).

Several techniques are used for introducing lipids into edible films: they can be the only constituent of the film, they can form a layer over a hydrocolloid layer, or they can form an emulsion with the hydrocolloid.

Many authors (22,26,30–33) observed that edible waxes are significantly more resistant to water-vapor migration than most other lipid or nonlipid films. This great resistance of wax coatings is related either to their hydrophobic character (absence or low level of polar groups) or to their molecular orga-

TABLE 2
Water-Vapor Permeability of Lipid-Based, Polysaccharide-Based, and Protein-Based Films

Film	T (°C)[a]	ΔHR (%)[b]	l (µm)[c]	Permeability (10^{-11} g·m^{-1}·s^{-1}·Pa^{-1})	Reference
Lipid-based					
Myristic acid ($C_{14:0}$)	23	12–56	50	3.47	35
Palmitic acid ($C_{16:0}$)	23	12–56	50	0.65	35
Stearic acid ($C_{18:0}$)	23	12–56	50	0.11–0.22	35
Paraffin wax	23	0–85	150	0.03–0.06	38
Candelilla wax	25	0–100	100	0.018	61
Peanut oil	25	22–44	230	13.8	62
Hydrogenated cotton oil	27	0–100	1560	0.13	63
Cocoa butter	25	22–44	60	3.6	62
Polysaccharide-based					
MC[d]	25	0–52	25	8.7–14.0	64,65
HPMC[e]	27	0–85	190	10.5	65
Protein-based					
Gluten + glycerol	25	0–100	/	4.4–13.2	66
Soja proteins	25	50–100	65	179–304	67
W-prot.[f] + PEG 400[g]	25	0–63	115	150	34
Na-cas[h]	25	0–100	50	15.5–32.7	34

[a] T (°C), temperature during transfer.
[b] ΔHR, relative humidity gradient.
[c] l, thickness.
[d] MC, methylcellulose.
[e] HPMC, hydroxypropylmethylcellulose.
[f] W-prot., whey proteins.
[g] PEG, polyethyleneglycol 400.
[h] Na-cas, sodium caseinate.

nization (waxes present a tight orthorhombic crystalline arrangement that is perpendicular to the direction of the gas flow). This structure explains why pure *n*-alkanes, with a parallel to the flow arrangement, are less efficient as water-vapor barriers (26).

In general, permeability to water vapor and to oxygen decreases as the chainlength of lipids increases. For instance, McHugh and Krochta (34) showed improved moisture-barrier properties when the hydrocarbon chainlength was increased up to 16–18 carbons for fatty alcohols and monoglyc-

TABLE 3
Water-Vapor Permeability of Composite Films

Film	T (°C)[a]	ΔHR (%)[b]	l (µm)[c]	Permeability (10^{-11} g·m^{-1}·s^{-1}·Pa^{-1})	Reference
Bilayer systems					
MC[d] + paraffin wax	25	22–84	87	0.2–0.4	62
MC + beeswax	25	0–100	100	0.058	61
MC + carnauba wax	25	0–100	100	0.033	61
MC + candelilla wax	25	0–100	100	0.018	61
HPMC[e] + stearic acid	27	0–97	19	0.12	68
Emulsified systems					
MC + PEG[f] + myristic acid	23	12–56	50	3.5	35
HPC + PEG + AM[g]	21	0–85	150	8.2	69
Gluten + AM	23	0–11	65	5.6–6.6	70
Gluten + oleic acid	30	0–100	50	7.9	22
Gluten + soja lecithin	30	0–100	50	10.5	22
Na-cas[h] + AM	25	0–100	80	18.3–42.5	71
Na-cas + beeswax	25	0–100	104	11.1–42.5	71
W-prot.[i] + palmitic acid	25	0–90	140	22.2	34
W-prot. + stearic alcohol	25	0–86	150	53.6	34
W-prot. + bees wax	25	0–90	170	23.9–47.8	34

[a] T (°C), temperature during transfer.
[b] ΔHR, relative humidity gradient.
[c] l, thickness.
[d] MC, methylcellulose.
[e] HPMC, hydroxypropylmethylcellulose.
[f] PEG, polyethyleneglycol 400.
[g] AM, acetylated monoglycerides.
[h] Na-cas, sodium caseinate.
[i] W-prot., whey proteins.

TABLE 4
Water-Vapor Permeability of Synthetic Films

Film	T (°C)[a]	ΔHR (%)[b]	l (μm)[c]	Permeability (10^{-11} g·m^{-1}·s^{-1}·Pa^{-1})	Reference
Cellophane	25	22–84	20	5.6	62
Cellulose acetate	25	0–100	150	3.2	63
PVC[d]	25	0–100	100	0.068	63
LDPE[e]	38	0–90	25	0.07–0.097	72
HDPE[f]	25	0–100	100	0.01	63

[a] T (°C), temperature during transfer.
[b] ΔHR, relative humidity gradient.
[c] l, thickness.
[d] PVC, polyvinylchloride.
[e] LDPE, low density polyethylene.
[f] HDPE, high density polyethylene.

erides. For fatty acids, barrier properties were augmented with an increase of chainlength from 12 to 18 carbon atoms, but from 18 to 22, barrier properties decreased (35). This behavior could be explained by the differences in network tortuosity. Morphological arrangement of the fatty acid chains with respect to the polymers affects the barrier properties of the film. Chitosan-lipid-based films display better efficiency against moisture transfer when the lipid is uniformly incorporated in the matrix, such as films that contain lauric acid (36). Indeed, lauric acid exists in a crystal form that is conformational with the chitosan polymer, while other fatty acids do not fit within the chitosan structure.

Additionally, other researchers (31,37,38) have reported that the barrier properties increased with the degree of saturation of the lipid: films with paraffins and beeswaxes are more resistant than those prepared with polyunsaturated corn oil (38). They explained this behavior in terms of the relative water-vapor solubility in the liquid lipid and solid lipid phases and/or on the molecular organization of the lipid. Martin Polo *et al.* (26) showed that for paraffin and alkane-based films, the greater the size or the number of the fat crystals, the more the permeability was reduced. They also noted the role of the liquid phase to depend on the morphology or type of the solid hydrophobic material. For pure alkanes, the liquid is able to overcome or mask the imperfections of the crystalline solid arrangements [water-vapor transmission rate (WVTR), decreases slightly from 100 to 25% of solid material]; however, for paraffin wax, paraffin oil acts as a diluent, and the paths between crystals become more and more numerous for water-vapor molecules to pass through as the liquid phase is increased (from 100 to 25% of the solid content, WVTR remains nearly constant). This result can be used to overcome the problem of a film's rigidity, like wax-made films, by using liquids up to a certain threshold to improve flexibility.

Kester and Fennema (39,40) showed the influence of polymorphism of lipids in permeability: resistance to water-vapor and oxygen transport decreased upon conversion from the α (hexagonal) to the β′ form (orthorhombic) and then increased substantially upon conversion to the β form (greater solid-state density). They observed that stearyl alcohols were more resistant to permeability than tristearin, beeswax, and acetylated monoglycerides because of their ability to crystallize as compactly overlapping platelets with their planes normal to the direction of penetrant diffusion.

The water-vapor barrier efficiency depends on the polarity of lipids as observed by Fennema *et al.* (28): tristearin and stearic acid were less efficient than stearic alcohol because carbonyl and carboxyl groups are more polar than hydroxyl groups and they can form a water layer around them. Moreover, water-vapor permeability drops with an increase of hydrophobic compound content. For example, Kamper and Fennema (38) found that increasing the stearic acid concentration in the emulsified films decreased their water-vapor permeability until an optimum was reached.

The ability of a hydrophobic substance to retard moisture transfer depends also on the homogeneity of its final repartition in the supporting matrix and/or surface (19,30,33,36,38). Martin Polo *et al.* (33) showed that the least efficient films to retard the movement of water corresponded to the highest heterogeneous systems, independent of the nature of the substance; the most efficient barrier was obtained with homogeneous repartition of paraffin wax over a hydrophilic matrix. The same results were obtained by Debeaufort *et al.* (41) who showed that a film of laminated paraffin wax on a methylcellulose support (regular surface) was a 10-fold more efficient barrier to water-vapor transfer than an emulsified film (irregular surface). On the contrary, Kamper and Fennema (38) observed a greater capacity to retard the transfer of water vapor in emulsified films. This could be explained in terms of the different nature of lipids used (a blend of stearic and palmitic acids) and because of their different arrangement at the interface (emulsion) and surface (bilayer).

Greener Donhowe and Fennema (42) showed that a beeswax layer over a methylcellulose layer, deposited from a molten state, had a more uniform surface and tended to be a better barrier to water vapor than when laminated from an ethanolic solution. Where the solvent evaporates, some holes and pores are formed. Bilayer films, composed of gluten and waxes, have better moisture barrier properties than polyethylene (43), whereas monoglyceride esters alone provide less efficient bilayer films, but mixtures of monoglyceride esters and waxes perform better.

Concerning emulsified films, a more homogeneous distribution and smaller-size globules gave better barrier performances, but only when films were dried slowly (19).

Usually, the mechanical properties of films depend on the ability of the film-forming substances to form strong and/or numerous molecular bonds between chains. For a bilayer film, made of methylcellulose and paraffin wax/oil or hydrogenated palm oil/triolein, only the polymer is responsible for mechanical resistance and deformability; neither the lipidic nature (alkanes or triglycerides) nor the solid/liquid proportion nor the thickness changes the organization of the polysaccharide network and its physical properties (44). Moreover, some lipids (acetoglycerides, fatty acids, monoglycerides, phospholipids) are used to increase the flexibility of polymeric films. They can be considered plasticizers because they weaken the intermolecular forces between adjacent polymer chains. Unfortunately, this produces an increase in gas and water-vapor permeability across the film.

Some factors, such as humidity and temperature, can influence the structure and the physical state of lipids and, consequently, their water-vapor barrier efficiency. Water is the most common plasticizer. At high relative humidity, the polar groups of fatty acids and fatty alcohols in wax, which are sandwiched between aliphatic chains under normal conditions, may be able to humidify the film sufficiently to influence its water-vapor permeability (45). Permeability depends on diffusion (kinetic factor) and on sorption (thermodynamic factor) of the penetrant. Generally, an increase of temperature causes an increase of diffusion owing to an increase of molecular thermal motion; on the contrary, water sorption is favored by a decrease in temperature. Delporte (44) found also that a change of the physical state of the lipid can influence water-vapor permeability. When the lipidic layer of a bilayer film passes from a solid state to a more liquid state, permeability increases with temperature; on the contrary, when no physical state change occurs, permeability decreases with an increase in temperature.

Kamper and Fennema (18) observed that, for a bilayer film of stearic and palmitic acids and hydroxypropyl methylcellulose at temperatures lower than 25°C (5 and −19°C), WVTR increased as temperature was decreased, probably owing to shrinking and breaking of the film as the components became more rigid. This also may be due to an increase of film hydration at lower temperatures, thus facilitating moisture transfer through the film. Noguchi (46) reported that hydration around polar groups increased with decreasing temperature and that hydration around biopolymers (such as polysaccharides) near 0°C should be twice that at room temperature. Fox (47) observed that an increase of the working temperature (23–35°C) and length of storage (5–35 d) induced healing and recrystallization, which produced larger and closer-packed plate crystals that were oriented parallel to the plane of the base sheet and so increased the efficiency against moisture transmission. Kester and Fennema (48) found the same result for stearyl alcohol films layered on a filter paper support.

Applications of edible packagings. Applications of edible films are numerous and different: they provide protection to moisture and oxygen between the food and the environment and between different parts in a heterogeneous food; they improve mechanical handling and enhance the food appearance. Edible films also can be used as carriers of fungicides, antioxidants, antimicrobial agents, coloring agents, flavoring agents, vitamins, nutrients, and growth regulators (49).

In the literature, much work can be found concerning edible films that contain lipids; most of them deal with coating of fresh fruits and vegetables (15–17,50). The ability to control desiccation and oxidation during carriage and storage (mostly for tropical fruits), to incorporate fungicides for decay control or growth regulators, to improve appearance by imparting shine to the surface, and to control aspects of product physiology all serve to lengthen the market window for commodities with a finite shelf life (51). Usually, natural waxes (carnauba, candelilla, beeswax) or paraffin, oxidized polyethylene, also in combination with other lipids, resins, or polysaccharides are used. Care must be taken to allow adequate respiration for normal ripening. Excessive coating can affect the normal maturation process, triggering anaerobic respiration and shortened shelf life. For example, for fruits such as oranges, this can cause an increase in ethanol, acetaldehyde, and off-flavors in the final product (52). Films also can be used for coating lightly processed fruits and vegetables. Krochta *et al.* (53) reported that films made from an aqueous emulsion of casein with acetylated monoglycerides reduced moisture transmission of fruit slices; treated with a buffer solution at the isoelectric point of casein, films became insoluble in water; when the buffer was made with ascorbic acid, the film had the potential of providing antioxidant properties.

Dried fruits too can be waxed or oiled to retard further loss of moisture, which could result in surface crystallization of sugar or development of an unacceptable texture; such coatings also may inhibit the development of insect eggs or larvae under the fruit surface (54). Surfactants, such as ethyl esters of fatty acids (C_{10}–C_{18}), have been used to coat grapes and plums to increase the drying rate in the manufacture of raisins, prunes, and other waxy fruits (55).

Edible coatings with lipids are currently also used for frozen foods, such as meat and fish. Coatings of low-melting-point acetylated monoglycerides, used alone or after applying a whey protein isolate solution, were effective in reducing the rate of moisture loss of frozen king salmon by 42–65% during the first 3 wk of storage at −23°C (20). A product called Myvacet (Eastman Chemical Products, Inc., Kingsport, TN) is a distilled acetylated monoglyceride protective coating for frozen poultry. Applied as a dip or spray prior to freezing, the coating may be left on the product during cooking (51). The Ambrosia Chocolate Company (Milwaukee, WI) developed a water-in-oil emulsion as a flavor carrier and protective containment for meat. The benefits of this coating included increased yield (2–6% less cook-out loss), decreased moisture loss during storage (2–17% less for coated samples), flavor improvement and innovation, production efficiency owing to high speed and continuous application, and improvement in meat tenderness (56). Another water-in-oil emulsion for frozen meat products has been patented (57); fats used included corn oil, cottonseed oil, sunflower seed oil, soybean oil, and fat from chicken, beef, or pork.

Another example of lipid coating is the use of paraffin wax for preventing weight loss and reducing the air space in eggs (58). Moreover, solid fats, such as cocoa butter, palm oils and waxes, can be used to cover confectionery products.

Edible films can also be placed between two food components with different water activities for storage purposes: bilayer films of stearic–palmitic acid and hydroxypropyl methylcellulose, placed between tomato paste and crackers, may stabilize the initial moisture gradients during storage at different temperatures. The films were undetectable after the foods were heated prior to consumption (18). Rico-Peña and Torres (59) found that a bilayer film of methylcellulose and palmitic acid retarded moisture transfer from ice cream to a sugar cone, keeping its crispness longer than 3 mon, which was the commercial storage life of the uncoated product.

Finally, beeswax and vegetable oil were extending the shelf life of raisins stored with cereals (31,60).

In this work, we discussed the importance of lipids in biopackaging, in particular in edible films. Lipids are used for their hydrophobic character as water-vapor barriers. Their efficiency depends not only on chemical structure, degree of saturation, and physical state but also on their homogeneity in the film. A bilayer film is a better barrier than an emulsion film. Lipids in general have no influence on the mechanical properties of films, but some of them (acetoglycerides, fatty acids, monoglycerides, phospholipids) often are used in the formulation as plasticizers. They increase flexibility by weakening the intermolecular forces between adjacent polymer chains.

In general, edible films have lower barrier and mechanical properties than plastic films, but their main advantage is that they can be eaten and no waste is made or, if left in the environment, they are totally nonpolluting because they are biodegradable products. For this main reason, more and more industries have recently become interested in the use of edible films.

Currently, edible film research is trying to find new formulations that contain lipids to improve biopackaging performance that can compete with classical synthetic packagings.

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