

Chapter 13

Mechanical and Permeability Properties of Edible Films and Coatings for Food and Pharmaceutical Applications

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13.1 Introduction

Use of natural polymers, such as proteins and polysaccharides, as coating or film materials for protection of food has grown extensively in recent years. These natural polymers can prevent deterioration of food by extending shelf life of the product and maintaining sensory quality and safety of various types of foods (Robertson 1993). Generally, film and coating systems are designed to take advantage of barrier properties of polymers and other molecules to guard against physical/mechanical impacts, chemical reactions and microbiological invasion. In addition, the use of natural polymers presents added advantages due to their edible nature, availability, low cost and biodegradability. The latter particularly is of paramount interest due to demand for reducing the amount of non-biodegradable synthetic packaging. Furthermore, these polymers can be easily modified in order to improve their physicochemical properties for filming and coating applications.

Edible films are freestanding structures, formed and applied for specific packaging uses. Edible films can be used to maintain separation of various components within a single food product or applied directly to the external surface of a food to inhibit migration of moisture, oxygen, CO₂, aromas, lipids, etc. Use of edible films and coatings for separating different components in multi-component foods can improve the quality of a food product (Krochta and De Mulder-Johnston 1997). Edible films with adequate mechanical properties can conceivably also serve as edible packaging for select foods (Krochta and De Mulder-Johnston 1997). They are formed by casting and drying film-forming solution on a leveled surface; drying a film-forming solution on a drum drier; or using traditional plastic processing techniques, such as extrusion. However, it is also possible for an edible film to be formed by applying coating solution directly at the surface of a food.

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Film requirements for foods are complex. Unlike inert packaged commodities, foods are often dynamic systems with limited shelf life and very specific packaging needs. In addition, since foods are consumed to sustain life, the guarantee of safety is a critical dimension of their packaging requirements. While issues of food quality and safety are first and foremost in the mind of the food scientist, a range of other issues surrounding development of any food package must be considered before a particular packaging system becomes a reality. Secondary packaging is often used to provide additional physical protection to the product. It may be a box surrounding a food packaged in a flexible plastic wrap. It could also be a corrugated box containing a number of primary packages for the purpose of easing handling during storage and distribution, improving stackability, or protecting primary packages from mechanical damage during storage and distribution.

Coatings are defined as thin layers of material applied to the surface of a food. Its purposes may be to provide a barrier against migration of moisture, oxygen (O_2), carbon dioxide (CO_2), aromas, lipids, etc., to carry functional food ingredients (e.g., antimicrobials, antioxidants, and flavor components), and/or to improve mechanical integrity or handling of the food product. In addition to increased barrier properties, edible films and coatings control adhesion, cohesion and durability to improve appearance of coated foods (Krochta 1997). Thus, coatings preserve attributes associated with food quality, as well as increase shelf life (Kester and Fennema 1986). Edible coatings also have potential for maintaining quality of a food after primary packaging is opened, by protecting against moisture change, oxygen uptake and aroma loss (Krochta 1997). Edible coatings form an integral part of the food product, and hence should not adversely impact on sensory characteristics of the food (Guilbert et al. 1996). Also, to be accepted commercially, components of an edible film should be generally recognized as safe (GRAS).

Edible coatings are applied and formed by addition of a liquid film-forming solution directly onto the food product. They may be applied with a paintbrush, by spraying, dipping or fluidizing (Cuq et al. 1995). Application of edible coating to meat and fish products may be produced by dipping, spraying, casting, rolling, brushing or foaming (Donhowe and Fennema 1994). Coatings used for meat products must have appropriate moisture barrier properties, water or lipid solubility, color, appearance, mechanical and rheological characteristics. Use of composite coatings may be necessary to improve gas exchange, adherence to coated products and moisture vapor permeability (Baldwin et al. 1995). Addition of vegetable oils can improve coating moisture barrier properties, while addition of glycerol, polyethylene glycol, and sorbitol can reduce film brittleness. Sealing meat with cross-linked sodium caseinate gel effectively preserved color of fresh meat, eliminated need for absorbent pads, and produced a juicer product by reducing drip loss (Ben and Kurth 1995). Thus, coated foods may not require high-barrier packaging materials, allowing the entire packaging structure to be simplified. Edible films and coatings can also incorporate active ingredients such as antioxidants, antimicrobial agents, colorants, flavors, fortified nutrients and/or spices (Floros et al. 1997). A composite film containing these active compounds can prevent rancidity and improve shelf life by controlling bacterial proliferation.

In summary, functional properties of an edible film or coating will be directly related to the composition and structure of its components. These parameters should be adapted appropriately so that functional properties of the film or coating are preserved through all processing, transport and storage conditions associated with a particular food. The challenge for successful use of biodegradable films and coatings is to stabilize their functional properties and adapt their mechanical properties in accordance with the intended application.

13.2 Film and Coating Composition, Structure and Functionality

Preparation of edible packaging generally involves addition of proteins, polysaccharides, plasticizers, lipids, and sometimes other components. Composite films may be heterogeneous in nature, and can be formed via mixtures of these materials. This approach allows for better exploitation of the unique functional properties inherent to each of the film's individual components.

According to Cuq et al. 1998, preparation of protein-based films requires formation of a continuous, low-moisture, and a more or less ordered macromolecular network, consisting of numerous and uniformly distributed interactions between polymer chains. The probability of forming intermolecular bonds mainly depends on shape of the protein (fibrous vs. globular) and on physicochemical conditions during processing. High molecular weight proteins (e.g., myosin) and fibrous proteins (e.g., myosin and F-actin) generally form films with good mechanical properties, while globular or pseudo-globular proteins (e.g., G-actin) need to be unfolded before film formation. Myofibrillar proteins are soluble in dilute salt solution or in low ionic strength solutions at neutral pH. Because of the hydrophilic nature of proteins, edible films made from them have an excellent oxygen barrier property, but they are susceptible to moisture (Gueguen et al. 1998; Stanley et al. 1994; Stefansson and Hultin 1994).

Proteins films are generally brittle and susceptible to cracking due to the strong cohesive energy density of the polymers (Lim et al. 2002). Addition of compatible plasticizers improves extensibility and viscoelasticity of films (Brault et al. 1997). According to Ressouany et al. (1998), protein based films containing sorbitol produce films with higher viscoelasticity. However, when polyethylene glycol and mannitol were added, a lower plasticizing effect was observed and more rigid films with lower elasticity properties were produced.

Edible coatings can be made from a variety of polysaccharides derived from plants (pectin and cellulosic derivatives), seaweed extracts to connective tissue extracts of crustaceans (alginate, chitosan, carrageenan) or bacteria (pullulan, levan, elsinan). Such coatings have been used to retard moisture loss of some foods during short term storage. However, polysaccharides, being hydrophilic in nature, do not function well as physical moisture barriers. The method by which they retard moisture loss is by acting as a sacrificial moisture barrier to the atmosphere, so that

moisture content of the coated food can be maintained (Kester and Fennema 1986). In addition to preventing moisture loss, some types of polysaccharides films are less permeable to oxygen. Decreased oxygen permeability can help preserve certain foods.

Due to the hydrophilic nature of polysaccharide, polysaccharide-based films exhibit limited water vapor barrier ability (Gennadios et al. 1997). However, films based on polysaccharides like alginate, cellulose ethers, chitosan, carrageenan or pectins exhibit good gas barrier properties (Baldwin et al. 1995; Ben and Kurth 1995). The gas permeability properties of such films result in desirable modified atmospheres, thereby increasing shelf life of the product without creating anaerobic conditions (Baldwin et al. 1995). Polysaccharide films are used in Japan for meat products, ham and poultry packaging before smoking and steaming processing. The film is dissolved during the process and the coated meat exhibits improved yield, structure and texture and reduced moisture loss (Labell 1991; Stollman et al. 1994).

Multi-component edible films and coatings consisting of blends of various polymers, polysaccharides, proteins and/or lipids have been developed to have cooperative functionalities. Polysaccharides can produce structural cohesion to provide a supporting matrix. Proteins can also provide structural cohesion, while lipids contribute a hydro-repulsive character to a film (Wu et al. 2002). For example, under certain conditions, addition of a polysaccharide to a protein film formulation can improve moisture barrier resistance and mechanical properties of a film (Letendre et al. 2002a; Ressouany et al. 1998). These enhanced properties may be due in part to formation of cross-links between film components (Thakur et al. 1997) or formation of complexes between protein and polysaccharide constituents (Letendre et al. 2002a; Sabato et al. 2001; Thakur et al. 1997; Shih 1994; Imeson et al. 1977). Strong interaction between two components resulting with a higher bounded β -structure (β -sheet and β -strand content), a more ordered structure and a cross-linked protein-polysaccharide network was obtained after heating and irradiation treatment of caseinate-whey based films in the presence of carboxymethyl-cellulose (CMC). These structural modifications led to more rigid films with improved mechanical strength and barrier properties (Cieřla et al. 2006a, b; Letendre et al. 2002a, b; Le Tien et al. 2000).

13.3 Mechanical Properties

Many food proteins such as casein, wheat gluten, soy or whey isolate, and polysaccharides such as alginate, starch, cellulose, cassava starch or pectin, have been formulated into edible films or coatings (Henrique et al. 2007; Tapia et al. 2007; Letendre et al. 2002a; Le Tien et al. 2000; Vachon et al. 2000; Sabato et al. 2001). However, the highly hydrophobic nature of these proteins limits their ability to provide desired edible film functions.

Mechanical or physicochemical properties of films can be improved by application of extrusion or promotion of reaction between film components. Physical (heating, irradiation, pressure, ultrasound), chemical (chemical cross-linking, acids, alkali) or enzymatic treatments can improve functional properties of films (Conca 2002; Letendre et al. 2002a; Rhim et al. 1999; Yildirim and Hettiarachchy 1998; Stuchell and Krochta 1994). Cross-linking between proteins and polysaccharides, as well as other treatments used to improve interactions between these two types of macromolecules, may be used to improve functional properties and resistance of protein-based films (Letendre et al. 2002a; Le Tien et al. 2000; Ressouany et al. 2000; Mezgheni et al. 1998b). For example, pectin may form cross-links with proteins under certain conditions (Thakur et al. 1997). Autoclaving enhances protein–polysaccharide, pectin–protein and agar–protein interactions, resulting in a three-dimensional network with improved mechanical properties (Letendre et al. 2002a, b). According to Thakur et al. (1997), high temperatures generate a less ordered structure, making more functional groups available. According to Letendre et al. (2002b) when calcium, whey proteins and polysaccharide are mixed together, a fully disordered and dissociated polymer chains could interact more favorably together. The addition of glycerol in a film formulation reduces interactions between the protein and water (Letendre et al. 2002b). It is possible that hydrophilic structure of glycerol might be involved in associations with hydrophilic sites of proteins (H-bonding), thus limiting protein hydration i.e., protein–water interaction. The presence of plasticizers can enhance formation of protein cross-links. It was observed by Brault et al. (1997) and Mezgheni et al. (1998a) that the presence of glycerol, propylene glycol or triethylene glycol in caseinate based – film formulations enhanced formation of cross-links during irradiation treatment. Environmental and processing conditions affect composition and structure of polymers, which directly affect functionality of the resulting films. For example, use of homogenization and microfluidization for particle size reduction of whey protein based film formulations resulted in an increase in the interfacial area, providing a stronger film with reduced water vapor permeability (Perez-Gago and Krochta 2001).

13.4 Barrier Properties

Barrier properties of edible films include water vapor permeability, gas permeability (O_2 and CO_2), volatile permeability and solute permeability. Both O_2 and CO_2 permeability is important when respiration or oxidation reactions could affect quality of the food (e.g., fresh or pre-cut fruits and vegetables). Water vapor permeability is an important factor to consider when crispness of a food needs to be maintained during storage. The volatile and solute permeability is an important property to control when diffusion of a compound is to be limited. Barrier properties of edible films prepared from polar polymers (e.g., polysaccharides) are sensitive to humidity. However, protein-based films traditionally have the worst barrier

properties (Cuq et al. 1995). Since lipid is an excellent moisture barrier, incorporation of lipid into a film can reduce water vapor permeability. The structure of the polymer chains and the lipid distribution within the matrix play a significant role in permeability of films. As described previously, a less ordered structure can permit better interactions between the polymers (Letendre et al. 2002b). The increase of cohesion between protein polypeptide chains and a uniform dispersion of lipid in the polymer matrix could also be effective for improvement of the barrier properties of films (Sabato et al. 2001; Perez-Gago and Krochta 2000). Molecular crystallinity also significantly affects permeability and the solubility of films. Lipids can be used in numerous crystalline forms. In general, higher the degree of crystallinity, the lower the permeability of a film (Perez-Gago and Krochta 2000; McHugh and Krochta 1994).

13.4.1 Gas Barrier Properties

Many foods require specific atmospheric conditions to sustain their freshness and overall quality during storage. Packaging a food product under a specific mixture of gases, known as modified atmosphere packaging (MAP), can help maintain quality and safety of such products. To ensure a constant gas composition inside the package, packaging material needs to exhibit certain gas barrier specificity. In most MAP applications, the gas mixture inside the package consists of carbon dioxide, oxygen or nitrogen, or some combination of these gases. Though scientific literature provides a vast amount of information on barrier properties of biomaterials, direct comparisons between different biomaterials are complicated and sometimes not possible, due to use of different types of equipment and dissimilar analytical measurements within various studies. A brief review of some of these literature reports is provided below.

Films based on polysaccharides, such as alginate, cellulose ethers, chitosan, carrageenan or pectin, generally exhibit good gas barrier properties (Baldwin et al. 1995; Ben and Kurth 1995). Addition of lipids or starch to a film formulation can improve both oxygen and oil barrier properties (Kroger and Igoe 1971; Morgan 1971; Sacharow 1972; Wu et al. 2002). The gas permeability properties of such films result in desirable modified atmospheres, thereby increasing the shelf life of the product without creating anaerobic conditions (Baldwin et al. 1995). Addition of a fatty acid through an emulsion with proteins can increase the O₂ and CO₂ permeability of the resulting film, while addition of acetylated monoglycerides actually provides the reverse effect (Wu et al. 2002).

The conventional approach to producing high-barrier edible films or coatings to maintain food in a protective atmosphere involves use of multilayers of different films to collectively obtain the required properties. An example of this multilayer approach might be a biobased laminate, consisting of an outer layer of plasticized chitosan film combined with another layer of polyhydroxyalkanoate (PHA) or alginate, to obtain an appropriate gas barrier.

Bilayer coatings, has been shown to reduce gas exchange, and result in higher internal carbon dioxide and lower oxygen concentrations in cut apple pieces (Wong et al. 1994). Unfortunately, little or no data exists showing the barrier property effects of bilayer coatings on whole fruits or vegetables.

13.4.2 Water Vapor Permeability

The predominantly hydrophilic character of natural polymers, including many proteins and polysaccharides, result in poor water barrier characteristics (Kester and Fennema 1986; Peyron 1991; Gennadios et al. 1997; McHugh 2000). According to Henrique et al. (2007), water vapor permeability (WVP) can be directly related to the quantity of –OH group on the molecule. Also, environmental conditions can significantly affect the WVP. In general, a high relative humidity (90% RH) and a low (–30°C) storage temperature improve WVP. For example, increasing the relative humidity gradient at a constant temperature increased transfer of moisture through films based on hydroxypropyl methylcellulose, stearic and palmitic acids (Kemper and Fennema 1984), and polyethylene which are more permeable to water vapor at –30°C than at 35°C (Labuza and Contreras-Medellin 1981). Polysaccharide films are used in Japan for meat products, ham and poultry packaging prior to smoking and steam processing. The film is dissolved during this process, and the coated meat exhibits improved yield, structure and texture, and reduced moisture loss (Labell 1991; Stollman et al. 1994). Perez-Gago and Krochta (2000) have investigated the effect of drying temperature on WVP of whey protein isolate based-films, and observed that WVP decreased significantly as drying temperature increased.

Lipids have a low affinity for water, and can significantly reduce the water vapor permeability (WVP) of films. For example, it was found that WVP of pure caseinate films could be reduced by over 70% through incorporation of lipid materials (beeswax) (Avena-Bustillos and Krochta 1993). However, the polarity of lipids used is an important factor to consider. Solid lipids, such as palm oil, stearic acid, beeswax or paraffin, yielded much smaller WVP values than cellulose ether based films containing liquid lipids, such as oleic acid (Wu et al. 2002). Fatty acids embedded within the cellulose ether matrix may function to enhance adhesion of the wax layer to the underlying film, thus, resulting in a bilayer film with a lower WVP (Wu et al. 2002). For films cast from aqueous, lipid emulsion solutions, the process is complex, and incorporation of lipids requires addition of emulsifying agents or surfactants to improve emulsion stability. Perez-Gago and Krochta (1999) showed that pH may also have an influence on film WVP. In protein-stabilized emulsions, as the net charge approaches zero at the protein isoelectric point (pI), electrostatic repulsion between emulsion droplets becomes weak, and probably a lowered lipid mobility due to protein–protein aggregation occurred and reduced interconnectivity among lipid droplets, resulting in a higher WVP. At pH values above and below the protein pI , droplets have a net charge and electrostatic repulsive forces are present between droplets. The best water barrier properties were

observed in protein films at neutral pH values (Perez-Gago and Krochta 1999; McHugh 2000). Decreased mean particle diameters of the emulsion or of the lipid particles resulted in linear decreases in WVP values (Perez-Gago and Krochta 2001; McHugh and Krochta 1994) although it is interesting to note that protein–lipid films are often difficult to obtain. For example, bilayer film formation requires the use of solvents and/or high temperatures, making production more costly. Furthermore, separation of the layers may occur with time.

Laminant films can be formed by applying another material (e.g., lipids) as a laminant over a polysaccharide-based film. Bilayer films, such as these, tend to delaminate over a period of time, developing pinholes or cracks, exhibiting poor strength and non-uniform surface and cohesion characteristics (Sherwin et al. 1998). Bilayers are often brittle, and not practical for use in many applications (Fairley et al. 1997). In addition, bilayers require multiple drying steps, whereas emulsion-based films require only one dehydration step (Debeaufort and Voilley 1995). Application of the lipid layer often requires use of solvents or high temperatures, making production more costly and less safe. However, bilayer films are desirable, in that they generally exhibit better barrier properties than emulsion films (Fairley et al. 1997; Sherwin et al. 1998). Chitosan/pectin laminated films can yield transparent films that exhibit increased resistance to water dissolution (Hoagland and Parris 1996). Yan et al. (2001) obtained similar results with chitosan/alginate laminated films. Additionally, these authors demonstrated that films prepared from low molecular weight chitosan were twice as thin and transparent, as well as 55% less permeable to water vapor, than those prepared with standard chitosan. The improved mechanical properties observed for these chitosan laminate films could be due to electrostatic interaction between carboxylate groups of pectin or alginate and the amino groups of chitosan (Dutkiewicz and Tuora 1992). Better WVP and mechanical properties were obtained after lamination of methylcellulose/corn zein–fatty acid films (Park et al. 1994). Laminated chitosan–cellulose and polycaprolactone films can be used in modified atmosphere packaging of fresh produce (Makino and Hirata 1997). Laminates with effective water barriers were also developed (Park et al. 1994) by coating a hot solution of corn zein with different types of fatty acids onto a methylcellulose-based film. Resulting films were water insoluble, and the WVP was reported to decrease as both length and concentration of the fatty acid increased. It is clear that homogeneous distribution of the hydrophobic material plays a key role in decreasing WVP in both emulsified and laminated film applications.

Increased cohesion between protein polypeptide chains is thought to improve moisture barrier properties of the protein-based films. For instance, cross-linking of proteins by means of chemical, enzymatic (transglutaminase) or physical treatments (heating, irradiation) was reported to improve water vapor barrier characteristics, as well as the mechanical properties and resistance to proteolysis, of protein films (Sabato et al. 2001; Ouattara et al. 2002; Ressouany et al. 1998, 2000; Brault et al. 1997). When cross-linked whey proteins are entrapped within a cellulose matrix, insoluble films with good mechanical properties, high resistance to proteolytic enzymes and decreased WVP are generated (Le Tien et al. 2000).

Food quality deterioration due to physicochemical changes or chemical reactions is often caused by mass transfer or between the food and its surrounding medium, or within the product itself. Compounds whose migrations need to be controlled are water, oxygen and flavor, with the main concern being water. Application of a coating containing hydrophobic substances (oils, fats, waxes, lacs, varnishes, resins, emulsifiers, essential oils, etc.) can be used to isolate or maintain separation of components differing in water activity within a composite food. Oils and fats are widely used in confectionery, cereal and dessert industries to prevent moisture absorption. Waxes are often used to coat fruits and vegetables in order to prevent desiccation during transport and storage. According to the literature, paraffin, candelilla, cellulose and beeswax are the most effective compounds for reduction of water vapor permeability ($0.02\text{--}0.06 \times 10^{-11} \text{ g m}^{-1} \text{ s}^{-1} \text{ Pa}^{-1}$), as compared to carnauba wax, glycerol, acetyl acylglycerols and myristic acid, for which a WVP of $1\text{--}148 \times 10^{-11} \text{ g m}^{-1} \text{ s}^{-1} \text{ Pa}^{-1}$ was observed (Lovegren and Feuge 1954; Greener and Fennema 1994; Koelsch and Labuza 1992; Hugon 1998). Emulsifiers can also be added to improve adherence, as a barrier to gas and moisture, or as an emulsifier (e.g., to permit good homogenization of essential oils) (Morillon et al. 2002). According to Karbowski et al. (2007), a thermal process may be used to favor formation of a bilayer structure in emulsion-based edible films, leading to better water barrier efficiency.

Bilayer coatings are the edible coatings or films of the future. The use of two polymer types allows beneficial properties of the two materials to be combined to create a superior film. Composite films of the future may consist of hydrophobic particles distributed within a hydrophilic matrix. Such a configuration could yield a water-soluble coating with good water vapor barrier properties (Baldwin 1991). Bilayer coatings, which already have been used to a limited extent, combine the water barrier properties of lipid coatings with the greaseless feel and good gas permeability characteristics of polysaccharide coatings.

Improvement of water vapor barrier properties represents a major challenge for the manufacturer of film and coating materials intended for food applications. When comparing water vapor transmittance of various natural polymers, it becomes clear that it is difficult to produce an edible film or coating with water vapor permeability rates compared to those provided by conventional plastics. If a high water vapor barrier material is required, there are very few biomaterials that can be used. Consequently, research efforts are currently focused on this problem with the realization that future biomaterials must be able to mimic water vapor barrier characteristics of conventional materials (Butler et al. 1996).

13.5 Solubility

As described previously, most biopolymers in their native states are sensitive to humidity, and are soluble in water (Vachon et al. 2000). Lipid components of edible origin can be incorporated into films and coatings to alter their susceptibility to water

(Greener and Fennema 1989; Martin-Polo et al. 1992; Debeaufort and Voilley 1995; Lacroix et al. 2001). However, composite films of proteins and lipids can decrease their water-solubility. As for good water vapor properties, a bilayer film would permit to obtain film with better water resistance. However, the process needs to be improved to obtain better stability. Good homogenization will be able to avoid separation of the layers.

Formation of cross-links between polymers can also reduce significantly solubility of edible film constituents. Vachon et al. (2000) was able to reduce the overall film solubility by more than 75% by promoting cross-linking through irradiation treatment. Incorporation of polycaprolactone into alginate-based films following immersion in calcium salt chloride (2 or 20%) decreased water-solubility of the film, exhibiting a recovery yield of 86% after water immersion for 24 h (Salmieri and Lacroix 2006). It is also expected that polymer–polymer interactions via hydroxyl and carbonyl (H-bonds or covalent reaction) moieties can enhance film insolubility (Salmieri and Lacroix 2006; Wang et al. 2001). When applied on beef, bologna or ham, such films were resistant to high humidity conditions, and were able to allow a controlled release of the active compounds (e.g., essential oils (Tables 13.1–13.3) from the film to the product during storage. Results of these studies have shown that the release rate of compounds from the film is related to calcium treatment and the food and essential oil composition (Oussalah et al. 2006a, b).

Other modifications can also be done to reduce solubility of biopolymer films. A functionalization agent may be incorporated onto a film or coating polymer to increase hydrophobicity of the polymer, and increase the insolubility and moisture barrier properties of the film. The functionalization agent may also increase mechanical properties of the film or coating. A functionalization agent can be defined as a substance that is covalently linked to the polymer matrix, with or without the aid of a coupling agent. Examples of functionalization agents include glyceraldehyde, acyl chlorides, fatty acids and anhydrides. Covalent modification of polysaccharides and proteins is generally accomplished via ester and ether linkages (Mezgheni et al. 1998a; Ressouany et al. 2000; Lacroix et al. 2001; Mulbacher et al. 2001; Brode 1991; Brode et al. 1991; Rutenberg and Solarek 1984). Use of cellulose xanthate as a matrix for entrapment of cross-linked whey protein can produce insoluble films with good mechanical properties, good stability and increased resistance to enzymatic attack (Le Tien et al. 2000). The potential application of these films used as packaging and wrappings can be of interest for various materials, and is probably compatible with several types of foods.

Le Tien et al. (2003b) and Lacroix et al. (2001) demonstrated that viability of lactic acid bacteria and the functionality of active compounds can be preserved when encapsulated in functionalized alginate (succinylated or *N*-palmitoylaminoethylated) or chitosan (succinylated), due to the film's insolubility and resistance to gastric fluid (Fig. 13.1). *N*-palmitoylaminoethyl alginate and *N*-acylated chitosan were also used to immobilize bioactive compounds (e.g., enzymes) to protect their bioactivity and to facilitate a controlled release of drugs over period of 30–90 h, depending on degree of functionalization (Le Tien et al. 2003a, 2004).

Table 13.1 Availability of total phenolic compounds or aldehydes in films containing essential oils during storage of meat at 4°C

Films ^b	Percentage of active compounds availability (%) ^a				
	Day 1	Day 2	Day 3	Day 4	Day 5
O + 2% CaCl ₂	100.00 a C	71.91 ± 2.13 b B	70.85 ± 1.82 c B	61.21 ± 4.64 c A	60.62 ± 4.65 c A
S + 2% CaCl ₂	a C	53.75 ± 0.28 a B	53.34 ± 2.18 b B	39.75 ± 2.39 b A	39.13 ± 4.44 b A
C + 2% CaCl ₂	a D	60.92 ± 6.74 a C	30.04 ± 1.19 a B	23.59 ± 3.37 a A	22.78 ± 0.28 a A
O + 20% CaCl ₂	100.00 a C	50.16 ± 4.40 b B	47.07 ± 1.74 b B	37.39 ± 2.71 b A	34.86 ± 1.89 b A
S + 20% CaCl ₂	a C	63.60 ± 1.20 c B	59.41 ± 2.48 c B	39.51 ± 2.38 b A	37.84 ± 1.93 c A
C + 20% CaCl ₂	A E	42.74 ± 3.57 a D	24.11 ± 2.06 a C	16.86 ± 0.85 a B	9.94 ± 0.35 a A

^aMeans for each treatment and in the same column bearing the same *lower case letters* are not significantly different ($p > 0.05$). Means in the same row bearing the same *upper case letters* are not significantly different ($p > 0.05$)

^bO films containing Spanish oregano essential oil; S films containing winter savory essential oil; C films containing Chinese cinnamon essential oil. Alginate based edible films were treated in 2 or 20% (w/v) of CaCl₂ solution

Table 13.2 Availability of main active compounds (total phenolic compounds or aldehydes) in films containing essential oils during storage of bologna at 4°C

Films ^a	Percentage of active compounds availability (%) ^b				
	Day 1	Day 2	Day 3	Day 4	Day 5
O + 2% CaCl ₂	100.00 a D	66.75 ± 3.96 c C	49.21 ± 2.06 b B	20.24 ± 1.32 c A	18.84 ± 0.68 c A
S + 2% CaCl ₂	a D	62.55 ± 1.23 b C	47.36 ± 3.27 b B	15.37 ± 1.08 b A	17.08 ± 0.22 b A
C + 2% CaCl ₂	a E	26.63 ± 1.30 a D	14.06 ± 1.47 a C	9.00 ± 0.69 a B	7.11 ± 0.33 a A
O + 20% CaCl ₂	100.00 a E	27.60 ± 0.94 b D	21.97 ± 1.86 c C	18.28 ± 0.38 c B	12.58 ± 0.97 c A
S + 20% CaCl ₂	a E	46.72 ± 1.78 c D	24.53 ± 1.07 b C	14.57 ± 5.73 b B	9.59 ± 0.43 b A
C + 20% CaCl ₂	a D	18.95 ± 0.36 a C	14.26 ± 1.50 a B	5.04 ± 0.33 a A	4.14 ± 0.45 a A

^a Alginate based edible films were treated with 2 or 20% (w/v) CaCl₂ solution. O films containing Spanish oregano essential oil; S films containing winter savory essential oil; C films containing Chinese cinnamon essential oil

^b Within each treatment and each column, means with the same *lowercase letters* are not significantly different ($p > 0.05$). Within each row, means with the same *upper case letters* are not significantly different ($p > 0.05$)

Table 13.3 Availability of main active compounds (total phenolic compounds or aldehydes) in films containing essential oils during storage of ham at 4°C

Films ^a	Percentage of active compounds availability (%) ^b				
	Day 1	Day 2	Day 3	Day 4	Day 5
O + 2% CaCl ₂	100.00 a C	83.04 ± 8.62 b B	37.08 ± 3.19 c A	34.25 ± 3.01 c A	33.65 ± 0.54 c A
S + 2% CaCl ₂	a E	80.10 ± 3.01 b D	27.61 ± 3.51 b C	21.70 ± 2.15 b B	11.09 ± 0.29 b A
C + 2% CaCl ₂	a D	37.75 ± 3.92 a C	15.56 ± 0.66 a B	15.41 ± 2.08 a B	4.35 ± 0.28 a A
O + 20% CaCl ₂	100.00 a D	49.77 ± 6.02 c C	47.79 ± 5.47 c C	32.46 ± 3.38 c B	21.65 ± 1.59 c A
S + 20% CaCl ₂	a D	32.51 ± 3.00 b C	32.03 ± 3.51 b C	22.79 ± 0.90 b B	14.10 ± 1.61 b A
C + 20% CaCl ₂	a D	20.47 ± 1.27 a C	19.14 ± 2.44 a C	12.04 ± 0.86 a B	3.64 ± 0.06 a A

^aAlginate based edible films were treated with 2 or 20% (w/v) CaCl₂ solution. O films containing Spanish oregano essential oil; S films containing winter savory essential oil; C films containing Chinese cinnamon essential oil

^bWithin each treatment and each column, means with the same *lowercase letters* are not significantly different ($p > 0.05$). Within each row, means with the same *upper case letters* are not significantly different ($p > 0.05$)

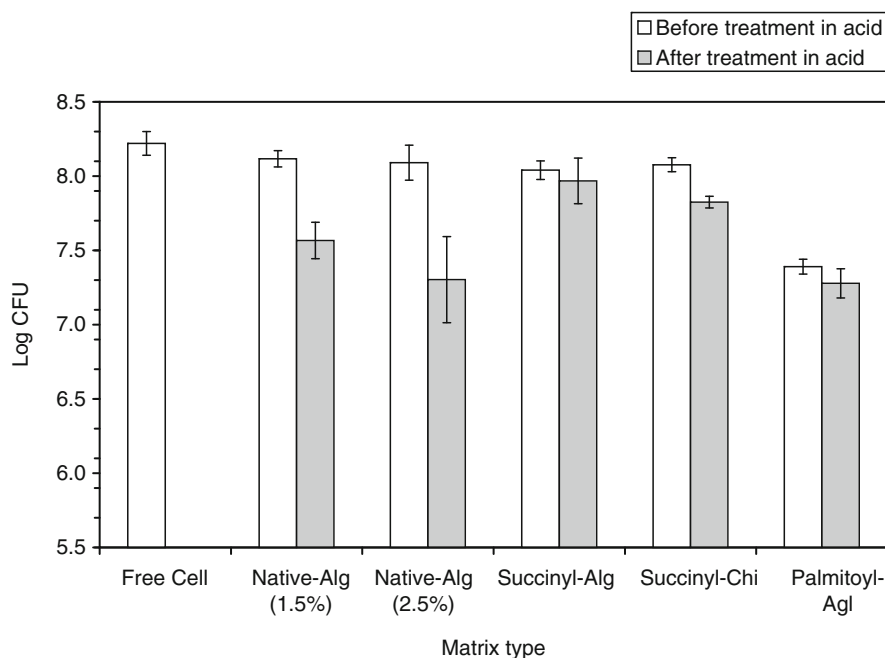


Fig. 13.1 Viability (%) of *L. rhamnosus* free and immobilized on different functionalized matrices and in simulated gastric fluid (pH 1.5) for 30 min (FC free cell; NA native alginate; SA succinylated alginate; SC succinylated chitosan and PA *N*-palmitoylaminoethyl alginate)

13.6 Thermal Properties

In the packaging industry, heat sealing is widely used to join polymer films (Mueller et al. 1998). In the heat sealing process, two films are presented together between heated plates or dies. As heat is applied, the surface of the crystalline polymer melts. Application of pressure results in interfacial interactions across joint surfaces to seal adjoining pieces of film. During cooling, a heat-sealed joint forms due to recrystallization of the polymer (Kim and Ustunol 2001). Seal strength is an indicator of seal quality. According to Lee 1994, modification of functional groups such as hydroxyl (OH), aldehyde (CHO), and carboxylic acid (COOH) moieties present in polyimide-based films, are responsible for the adhesion strength differences of various films. An increase in interactions between nitrogen- and oxygen-containing functional groups in polyethylene films is responsible for enhancement of seal strength (Possart and Deckhoff 1999). According to Kim and Ustunol (2001), hydrogen and covalent bonds involving C–O–H and N–C, may be the main forces responsible for sealed joint formation in films.

13.7 Potential Perspectives of Microemulsions and Bionanocomposites

Microemulsions have found numerous applications over a wide range of areas, including food systems (Flanagan and Singh 2006). However, application of microemulsions in foods systems is limited by the types of available surfactants, which are used to facilitate microemulsion formation. Microemulsions have attracted particular interest due to their ability to increase efficiency of antioxidants. Water-in-oil (w/o) microemulsions, formed with soybean oil and monoglycerides as the surfactant, were stable against oxidation for 70 days when 5% (w/w) ascorbic acid was incorporated into the water phase. When microemulsions were prepared without ascorbic acid, oxidative stability was reduced to less than 20 days (Moberger et al. 1987). A synergistic effect between ascorbyl palmitate and lecithin solubilized in the water phase, and α -tocopherol solubilized in the oil phase of the w/o microemulsion, were strongly synergistic in delaying peroxidation of lipid in fish oil (Hamilton et al. 1998).

Application of nanocomposites also promises to extend the uses of edible and biodegradable films (Sinha and Bousmina 2005). This new generation of composite films exhibits significant improvements in modulus, dimensional stability and solvent or gas resistance with respect to the pristine polymer. Nanocomposites also offer extra benefits like low density, transparency, good flow, better surface properties and recyclability. It is important to note that these improvements are obtained at very low filler contents (generally lower than 5% w/v). This enhancement of properties resides in fundamental length scales dominating the morphology of these materials, in which inorganic particles have at least one dimension in the nanometer (from 1 to 100 nm) range. It means that a uniform dispersion of these particles can lead to an ultra-large interfacial area between constituents. The very large organic/inorganic interface alters molecular mobility, relaxation behavior and consequent thermal and mechanical properties of the resulting nanocomposite material. Various inorganic nanoparticles have been recognized as possible additives to enhance polymer performance. Some examples of these particles are synthetic polymer nanofibers, cellulose nanowhiskers and carbon nanotubes. However, until now, only layered inorganic solids like clay have attracted some attention (Sorrentino et al. 2007). Only a few studies have suggested the possibility of incorporating nanoparticles to improve physical properties of food packaging. Mangiacapra et al. (2005) demonstrated the possibility of lowering diffusion of oxygen by adding clay montmorillonite to pectin to create nanocomposite materials. Nanocomposite films prepared from gelatin and montmorillonite exhibit significantly improved mechanical properties (Zheng et al. 2002). Coverage of nanocomposite films based on chitosan has demonstrated the increase in their stability during storage (Darder et al. 2003). These nanoparticles also can be used to stabilize food additives and efficiently control their diffusion into food. The controlled release of these compounds is important for long term storage of foods or for imparting specific desirable characteristics, such

as flavor, to a food system (Sorrentino et al. 2007). However, more studies should be done to assure the innocuity of nanomaterials with regard to human health. Development of this technology will likely further facilitate development of stable, functional and intelligent packaging systems. Also, use of nanomaterials will most likely enhance ability to produce more efficient active packaging systems.

13.8 Conclusions

Edible films and coatings have great potential for use in a wide variety of applications. They can be used to extend shelf life of fruits, vegetables, seafood, meat and confectionery products by preventing dehydration, oxidative rancidity, surface browning, oil diffusion and for their ability to modify internal atmosphere in fruits and vegetables. Moreover, when applied on fruits and vegetables, polysaccharide-based coatings can improve physicochemical, nutritional and sensorial properties of food products. Several studies have demonstrated that incorporation of active compounds, such as antimicrobials, antioxidants or bacteriocins, within edible films and coatings can improve microbial safety, shelf life and quality of meat, fish, fruit and vegetable products during storage. Development of new technologies (functionalization, cross-linking, nanomaterials, microemulsions, etc.) to further improve film properties (control release, higher bioactivities, bioactivity protection, resistance to water etc.) of active packaging, coatings or encapsulated materials represent a need for the future. The same may be needed as well for foods, nutraceutical, pharmaceutical and other applications.

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