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Edible moisture barriers: materials, shaping techniques and promises in food product stabilization

C. Bourlieu, V. Guillard, B. Vallès-Pamiès, N. Gontard

1 ENSAM-INRA Montpellier. Joint Research Unit Agropolymers Engineering and Emerging Technologies, claire.bourlieu@univ-montp2.fr
2 University of Montpellier II, Joint Research Unit Agropolymers Engineering and Emerging Technologies, valerie.guillard@univ-montp2.fr and nathalie.gontard@univ-montp2.fr
3 Nestlé Research Center Lausanne, Food Biopolymers, baltasar.valles-pamies@rdls.nestle.com

Abstract. Edible moisture barriers are effective alternatives to stabilize fresh or processed food products and satisfy consumers’ demand for long shelf-life products that are of good quality and nutritionally acceptable. This chapter deals with traditional and innovative film-forming materials and barrier technologies of edible films reported in scientific literature and patents over the last thirty years. The necessity of adopting an integrated approach in the development of edible moisture barriers to combine regulatory, nutritional, organoleptic and technical requirements is highlighted.

1 Introduction

The reduction of mass transfer between a food product and its surrounding atmosphere by coating the entire product with an edible material, is an extremely old practice, already used in the XII century in China (fruit waxing), and in England during the XVI century (meat larding) (Kester and Fennema 1986). Today, controlling mass, and more specifically moisture transfer, still remains an important challenge to maintain the quality of fresh or processed products, such as fruits, meats and seafood products. In ready-to-eat composite foods, the limitation of internal moisture transfer between components is also of major concern. It is all the more important as consumers’ demand for this kind of convenient product has increased. Moisture transfer from the “wet” to the “dry” component of these products affect the physical properties, specially texture, and chemical composition of the food system, and consequently, its quality and shelf-life (Katz and Labuza 1981).

The application of edible films and coatings can help reducing internal and external water transfer in slightly modified and processed food products (Debeaufort, Quezada-Gallo and Voilley 2000; Guilbert, Gontard and Gorris 1996; Guillard, Broyart, Bonazzi, Guilbert and Gontard 2003; Koelsch 1994). Edible protective films
or coatings can be defined as thin layers of material which are eaten by the consumer and provide a barrier to moisture, oxygen and/or solute movement in the food itself or between the food and its environment. Films are distinguished from coatings, since they are formed as stand-alone sheets of material whereas coatings are directly formed on the product. Edible films must have good barrier properties, but also, acceptable sensory characteristics (mouth feel, taste and aftertaste), a flexible and stretchable structure for an easy application onto the food and a composition conforming to the regulations (Guilbert 1986).

This chapter will point out the promises of edible moisture barriers in the protection of fresh or slightly modified products and in the design of ready-to-eat composite food products. After a review of the film-forming materials and shaping techniques, the discussion will focus on the barrier techniques of applications. The critical factors of these application techniques will be discussed.

2 Edible film-forming materials and principles of formation

2.1 Film-forming materials

Materials, properties and technologies of application of edible films have been extensively reviewed over the last thirty years (Anonymous 1997; Anonymous 2004a; Cuq, Gontard and Guilbert 1995; Daniels 1973; Debeaufort, Quezada-Gallo and Voilley 1998; Gontard and Guilbert 1994; Guilbert and Gontard 1995; Guilbert and Cuq 1998; Guillbert et al. 1996; Kester and Fennema 1986; Kroger and Igoe 1971; Morgan 1971; Nussinovitch 1998; Wu, Weller, Hamouz, Cuppett and Schnepf 2002). Materials which can be used to form edible films or coatings can classically be divided into three groups, which are presented in Table 1: proteins, polysaccharides and lipids and derivatives (Guilbert 1986; Kester and Fennema 1986).

Edible moisture barriers usually include lipids. Because of their apolar nature, these hydrophobic substances are capable of forming a water-impervious structure and reduce efficiently the water transfer. However, lipid-based materials are most of the time brittle so they are frequently combined with proteins and/or polysaccharides to improve their mechanical and structural properties (Wu et al. 2002). Several reviews focussing specifically on edible moisture barriers (Debeaufort et al. 2000; Koelsch 1994) and/or lipid-based edible films have been published (Baldwin, Nisperos, Hagenmaier and Baker 1997; Callegarin, Gallo, Debeaufort and Voilley 1997; Greener and Fennema 1992; Hernandez 1994; Quezada-Gallo, Debeaufort, Callegarin and Voilley 2000). The most recent review on lipid-based moisture barriers is that of Morillon, Debeaufort, Blond, Capelle and Voilley (2002).
An investigation in international patent databases (Anonymous 2006c) for deposited patents dealing with “edible moisture barriers” over the last 25 years, gave more than 50 answers. Of the total, 18% of the patents deal with the development of pure fat barriers, 58% with the development of a composite barriers including fat and other components (polysaccharides and protein derivatives or inorganic fillers), 13% with barriers based on pure hydrocolloids (protein or polysaccharides), 4% with sugar coatings, 4% with edible moisture barriers which can be based on any of the three kinds of components, and eventually 2% based on pure thin inorganic coatings. It is interesting to note that 25% of the patents directly describe the development of a composite food in which the edible film is supposed to be used.

A new class of barrier materials based on pure, thin (0.05 micron or less) amorphous inorganic coatings have been lately reported (Beyer, Jach, Zak, Jerome and Debrincat 1996). Such thin coatings overcome the textural problems associated with the use of organic coatings which have to be applied as a thick layer to be effective. The inorganic substance must be approved to be used in foods. In the United States, according to the section 21 of the Code of Federal Regulations for edible products (Anonymous 1977), authorized inorganic compounds are: silicon dioxide, single silicates, such as sodium silicate, calcium silicate and magnesium silicate, aluminium silicate, magnesium trisilicate, composite silicates such as sodium aluminium silicate, potassium aluminium silicate and calcium aluminium silicate, talc, clay materials such as bentonite, carbon, insoluble carbonates and phosphates. Even though the use of pure thin inorganic coatings as moisture barrier is still marginal, the possibility of using these materials as inorganic fillers in a barrier is also suggested in 8% of the patents. Edible inorganic compounds can thus be considered as a new category of edible coating materials.
Table 1. Polysaccharides, proteins, lipids and derivatives potentially used as film-former or barrier compound and their origin.

<table>
<thead>
<tr>
<th>Origin</th>
<th>Polysaccharides</th>
<th>Proteins</th>
<th>Lipids</th>
</tr>
</thead>
<tbody>
<tr>
<td>Botanical</td>
<td>Cellulose and derivatives (CMC, MC, HPC, HPMC); Starch and derivatives (fractionated: amylose, amylopectin, modified: propylated, acetylated…, hydrolysed starch: dextrins, maltodextrins, glucose syrups, pregelatinized starch); Pectin and pectinates; Alginates, agar, carrageenan, furcellaran; Gums (arabic, guar, locust bean, carob, karaya, adragant, tara, sterculia, tamarind, ghatti)</td>
<td>Corn zein; Wheat gluten and derivatives (gladins, glutenin); Soya proteins and derivatives (globulin 7S, globulin 11S); Rice and manioc proteins; Pea proteins; Peanut (comorachin), pistachio, cotton, sunflower, and rapeseed proteins</td>
<td>Native or hydrogenated palm, palm kernel, rapeseed, soya, peanut, coconut, castor, cotton oils, cocoa butter and their derivatives (obtained by fractionation, esterification, concentration and/or reconstitution: fatty acids and alcohols, mono-, di- and tri-glycerides, cocoa butter substitutes, margarine, shortenings, acetylated glycerides, lecithins, etc); Carnauba, candelilla, rice bran, and fruit (apple, bamboo, sugar, cane, citrus) waxes, jojoba oil; Wood rosin, tree lacs, citrus terpenes, gum lacs; Camphor, mint and citrus fruit essential oils; Liquorice</td>
</tr>
<tr>
<td>Animal</td>
<td>Chitin, chitosan.</td>
<td></td>
<td>Native or fractionated milk, tallow fats and their derivatives (obtained by fractionation, esterification, concentration and/or reconstitution: fatty acids and alcohols, mono-, di- and tri-glycerides, cocoa butter substitutes, margarine, shortenings, acetylated glycerides, lecithins etc); Beeswax, spermaceti*, chinese wax, shellac.</td>
</tr>
<tr>
<td>Microbial</td>
<td>Xanthan, dextran, pullulan, gellan</td>
<td>Chitosan</td>
<td>Paraffin, polyethylene wax, microcrystalline wax; Lignite, peat, montan waxes</td>
</tr>
</tbody>
</table>

*Formerly extracted from whale adipose tissue. No longer produced and sold in accordance with international regulations concerning whale capture. Now replaced by synthetic spermaceti made of pure cetyl palmitate or mixtures based on jojoba oil.
2.2. Methods of formation of edible barriers

Edible films and coatings are classically made following two main methods (Guilbert and Cuq 1998):

a) The “thermoplastic method” based on the thermoplastic properties of the film-forming material.

b) The “solvent method” based on a coacervation from a solution or a dispersion of the film-forming material in a solvent phase, followed by the evaporation of the solvent.

An example of these methods illustrated for lipids is shown in Fig. 1.

The thermoplastic method consists in shaping film-forming materials using thermal or thermo-mechanical processes in conditions of low hydration and induces structural transitions in the material such as melting of lipids and crystalline parts of polymers or a transition from the glassy metastable state to the rubbery state in the amorphous parts of the polymers (Guilbert and Cuq 1998). It is the most common procedure of forming lipid films and coatings. However, this method is less commonly used to shape hydrocolloids than the solvent method. The material is melted at an appropriate temperature or following a tempering schedule, and then it is solidified on a surface. Melting-solidification results in a dense crystalline network arrangement of the lipid material. High melting point lipids, such as waxes, require specific care since they solidify quickly. Therefore, they are often applied as emulsions or dispersions, using the solvent method to overcome this issue.

In the solvent method, the separation of the solubilised or dispersed material from the solvent phase can be explained by precipitation or phase change induced by solvent evaporation, addition of electrolyte, pH modification or heat treatment (Krochta and McHugh 1997). Such treatments can be adjusted to enhance film formation or specific properties. For composite emulsion-based films or coatings a lipid material and most likely a surfactant, is added to the solution, which is then heated above the lipid melting point and homogenised. The prepared solution is then applied on an appropriate support and the solvent evaporates.
Fig. 1. Methods of formation of edible lipid-based films by a) “thermoplastic” method, and b) the “solvent method”.

Films and coatings application techniques: casting, thermo-regulated spraying, dipping, falling-film, brushing, pan coating, fluid air bed.
2.3. Hydrophilic materials

Due to their hydrophilic nature, pure polysaccharide and protein films exhibit limited water vapour barrier ability. These coatings are thus favoured when other barrier properties are desired. Most of these films present interesting oil and gas (oxygen, carbon dioxide) barrier properties at low relative humidity (Albert and Mittal 2002). They are also characterized by good mechanical properties, specially those based on proteins which present a unique structure based on 20 monomers and a high intermolecular binding potential (Cuq, Gontard and Guilbert 1998). Hydrocolloid coatings can be applied in the form of high moisture gelatinous coatings, which delay moisture loss from coated foods by functioning as “sacrificing” agents rather than moisture barriers (Kester and Fennema 1986). They can also be chemically, enzymatically and/or physically treated to improve their moisture resistance (Ou, Wang, Tang, Huang and Jackson 2005; Tang, Jiang, Wen and Yang 2005).

The properties of various film-forming polysaccharides, such as alginates, pectins, starches, dextrins, cellulose, carrageenan, gums, chitosans and their derivatives, have been investigated for a long time and reviewed by Nisperos-Carriedo (1994). Their wide uses in the food industry have been favoured by their abundance, variability and low-cost, and are summarized in Tables 2a and 2b.

Several studies reviewed formulations, barrier properties and possible application of edible protein-based films (Table 3) (Gennadios, McHugh, Weller and Krochta 1994; Krochta and Mc Hugh 1997; Torres 1994). Overall, similarly to polysaccharide films, proteins exhibit relatively low moisture barrier properties, two to four times lower than conventional polymeric packaging materials (McHugh and Krochta 1994d). The limited resistance of protein films to water vapour transmission is attributed to their substantial hydrophilicity and to the amounts of plasticizers, such as glycerol and sorbitol, incorporated into films to impart adequate flexibility. The potential occurrence of adverse reactions to native proteins constitutes a huge limitation in the potential applications of various protein-based films (e.g. allergies to milk, egg white, peanut and soybean proteins, gluten…). Native proteins include two types of molecules: fibrous proteins, with structural water-insoluble groups and biologically active globular proteins. Generally, these globular proteins have to be modified, by heat treatment, pH modification or solvent addition, to obtain extended structures more susceptible to form a film.
Table 2a. Origin, film-characteristics and uses of polysaccharide-based edible films.

<table>
<thead>
<tr>
<th>Compound/Origin</th>
<th>Functional molecules</th>
<th>Film characteristics</th>
<th>Uses</th>
</tr>
</thead>
<tbody>
<tr>
<td>Starch (native or modified) / Various ubiquitous natural sources: tubers and cereals</td>
<td>Amylose: linear chain of D-glucose with α-1-4 links; Amylopectin: ramified chain with α-1-4 and α-1-6 links</td>
<td>Native starch: high susceptibility to hydration and low mechanical resistance; Amylose-based films: coherent, relatively strong, free-standing films; Amylopectin-based films: brittle and non-continuous (Zobel 1988)</td>
<td>Few applications of native starch; High amylose starch film widely used: extruded wraps, deep fried potato products, meat products (Gennadios, Hanna and Kurth 1997), refrigerated strawberries (Garcia, Martino and Zaritzky 1998a; Garcia, Martino and Zaritzky 1998b); Current tendency: alternative sources of starch with better physico-chemical and functional properties (Mali, Grossmann, Garcia, Martino and Zaritzky 2004; Mali, Grossmann, Garcia, Martino and Zaritzky 2005)</td>
</tr>
<tr>
<td>Cellulose (modified) / Structural polysaccharide of plants</td>
<td>D-glucose units β-1-4 glycosidic linkage; Native cellulose: crystalline water insoluble; Ethers: anionic (carboxymethyl cellulose) or non-ionic (methyl, hydroxypropyl) and hydroxypropyl methylcellulose). Relative hydrophilicity: HPC &lt; MC &lt; HPMC &lt; CMC. Water insoluble derivative: microcrystalline cellulose. Cellulose ether-based films: flexible and transparent, moderately strong, resistant to oil and fat migration and moderately barriers to moisture and oxygen (Arvanitoyannis and Yamamoto 1996; Arvanitoyannis and Biliaderis 1999; Park and Chinnan 1995)</td>
<td></td>
<td>Cellulose ethers-based films widely used: on pharmaceutical tablets, confectionery (Porter and Woznicki 1989; Woznicki and Grillo 1989), starchy fried products (Mallikarjunan, Chinnan, Balasubramaniam and Phillips 1997; Williams and Mittal 1999); Microcrystalline cellulose: filler in some coatings</td>
</tr>
<tr>
<td>Sodium alginate/ Brown seaweeds</td>
<td>Linear (1→4) linked polyuronic acid with 3 types of polymer segments: poly-β-D-mannuronic acid, poly-α-L-guluronic acid, blocks consisting of alternating D-mannuronic and L-guluronic acid residues (King 1983)</td>
<td>Reaction with several polyvalent cations to form gel; Films of increased water resistance obtained by immersion in CaCl2 solutions after formation (Rhim 2004)</td>
<td>Patented gelatinous coatings limiting moisture loss and oxidation (Earle 1968; Earle and McKee 1976); application to various meats (Allen, Nelson, Steinberg and McGill 1963a; Earle and McKee 1987; Lazarus, West, Oettinger and Palmer 1976); Carriers of antimicrobial agents: potassium sorbate and ascorbate or sorbic acid (Wong, Gregorski, Hudson and Pavlath 1996)</td>
</tr>
</tbody>
</table>
Table 2b. Origin, film-characteristics and uses of polysaccharide-based edible films

<table>
<thead>
<tr>
<th>Compound/Origin</th>
<th>Functional molecules</th>
<th>Film characteristics</th>
<th>Uses</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pectin / By product of citrus and apple productions</td>
<td>D-galacturonic acid polymers (α-1,4) with varying degrees of methyl esterification</td>
<td>Low-methoxyl pectins (esterification degree &lt; 50 %) capable of forming gel with calcium ions; Films with low moisture resistance obtained after drying</td>
<td>Few uses, reduction of stickiness and improved appearance of dry fruits and dates (Schultz, Owens and Maclay 1948; Schultz, Miers, Owens and Maclay 1949; Swenson, Miers, Schultz and Owens 1953);</td>
</tr>
<tr>
<td>Carrageenan / Red seaweeds</td>
<td>Sulphated polysaccharides of D-galactose and 3,6-anhydro-D-galactose. Number and position of sulphate groups on the disaccharide repeating unit determine classification in three major types: κ, τ, and λ. (Yuguchi, Thuy, Urakawa and Kajiwara 2002)</td>
<td>Thermoreversible gels produced from heated aqueous solutions; gelation promoted by the presence of cations (potassium, calcium and sodium)</td>
<td>Widely used: on fresh and frozen meat and fish to prevent superficial dehydration (Shaw, Secrist and Tuomy 1980), sausage casing (Macquarrie 2002), granulation-coated powder, dry solids foods, oily foods (Ninomiya, Suzuki and Ishii 1997), soft non gelatine capsules (Bartkowiak and Hankeler 2001; Fonkwe, Archibald and Gennadios 2003; Tanner, Getz, Burnett, Youngblood and Draper 2002)</td>
</tr>
<tr>
<td>Gums/ Botanical (arabic, guar) or Microbial (xanthan, gellan, etc)</td>
<td>Arabic gum most used: complex mixture composed of arabinoxylatans oligosaccharides and polysaccharides with a proteic part.</td>
<td>Arabic gum solutions present good adherence properties and form film upon drying.</td>
<td>Arabic gum: limitation of flavour evaporation (Nisperos-Carriedo 1994)</td>
</tr>
</tbody>
</table>
Table 3. Origin, film-characteristics and uses of the main kinds of protein-based edible films.

<table>
<thead>
<tr>
<th>Compound/Origin</th>
<th>Functional molecules</th>
<th>Film characteristics</th>
<th>Uses</th>
</tr>
</thead>
<tbody>
<tr>
<td>Collagen and derivatives (Gelatin) / Skin, tendon, and animal connective tissues</td>
<td>Fibrous proteins constituted of fibril sub-units</td>
<td>Collagen films formed by reticulations of amine and carboxyl groups; Gelatin-based films: flexible, clear, with good oxygen barrier properties, but poor moisture resistance; Classical formulations: 20-30 % gelatin, 10-30 % plasticizer and water.</td>
<td>Traditionally used in the meat industry: sausage casing and meat preservation early proposed in patents disclosures (Harvard and Harmony 1869); Various pharmaceutical and other food industry applications: ingredients micro-encapsulation, tablets and capsules (Gennadios et al. 1994)</td>
</tr>
<tr>
<td>Milk proteins/ By product of the milk and cheese manufacture</td>
<td>Casein (80 % of the total of milk proteins); Whey protein (20 % remaining of milk protein, solubility at pH 4.5); Total milk proteins</td>
<td>Casein films formed from aqueous solution without further treatment; Casein/glycerol (1:2) films: transparent, flavourless, flexible, highly permeable to moisture and very water soluble (Avena-Bustillos and Krochta 1993; Chen 1995; McHugh and Krochta 1994); Whey protein films: similar properties to casein films, but water insoluble. Heating required for their formation (disulfide bonds)</td>
<td>Sodium caseinates films tested as wrapping on bread: preservation of bread texture for 6 hours compared to control (Schou, Longares, Montesinos-Herrero, Monahan, O’Riordan and O’Sullivan 2005); Whey protein-based coatings widely used: breakfast cereals, raisins, frozen peas cheese pieces, micro-encapsulation of food additives...; Reduction of the textural perceptibility of whey protein film by mixing with sodium caseinate (Longares, Monahan, O’Riordan and O’Sullivan 2005)</td>
</tr>
<tr>
<td>Cereal proteins/ Corn, Wheat, Sorghum...</td>
<td>Non water (gluten) and alcohol soluble (prolamin) fractions from cereal proteins</td>
<td>Films based on corn zein and wheat gluten extensively studied; homogeneous, yellowish, relatively strong and water resistant wheat gluten film (ethanol dispersions/partial denaturation); Other film-forming cereal proteins studied (sorghum kafirin, rice bran)</td>
<td>Corn zein-based edible coatings widely used to extend the shelf-life of nuts by retarding, rancidity, staling and sogginess; Commercial uses for confectionery glaze and pharmaceutical tablets</td>
</tr>
<tr>
<td>Oilseed proteins/ Oilseed producing plants</td>
<td>Soy proteins most studied: globulin protein fractions (2S, 7S, 11S and 15S)</td>
<td>Flexible yellowish films with low moisture resistance properties formed from soy protein aqueous dispersions upon heating; Alkaline conditions reinforce film functional properties</td>
<td>Protection of various food products (nuts, aroma and flavours encapsulation, fresh meat, battered meat, etc) (Gennadios and Weller 1991)</td>
</tr>
</tbody>
</table>
2.4. Hydrophobic materials

The most commonly used hydrophobic film-forming barrier materials include (by decreasing order of efficiency):
- waxes
- lacs
- fatty acids and alcohols
- acetylated glycerides
- cocoa-based compounds and their derivatives

The classification of lipids by increasing efficiency can be explained by the chemical composition of the molecules (presence of polar components, hydrocarbon chain length, number of unsaturation or acetylation). For components having the same chemical nature, increasing chain length modifies the barrier properties because the polar part of the molecule decreases and does not favour water solubility in the film (McHugh and Krochta 1994d). The barrier efficiency of lipids also depends on their physical state (solid fat content at the temperature of use, crystalline form, etc). Indeed, many lipids exist in a crystalline form and each individual crystal is impervious to water vapour. Water flow permeates mainly between crystals and the intercrystalline packing arrangement has major consequences on the barrier properties of the material (Martini, Kim, Ollivon and Marangoni 2006). Consequently, migration rate can be slowed down to a certain extent by a proper tempering, which induces a more efficient structure against moisture migration. In the same way, in a continuous lipid phase, vapour migrates more easily in the liquid fat portion of the product. The solid fat content of the product at the temperature of application clearly influences the migration rate (Ghosh, Ziegler and Anantheswaran 2002; Kester and Fennema 1989c; Kester and Fennema 1989d).

Paraffin followed by candelilla wax and microcrystalline waxes, and eventually by beeswax, are considered as the most effective moisture barriers derived from edible waxes (Morillon et al. 2002). There is no satisfactory chemical definition for the term “wax” which is used for a variety of products of mineral, botanical and animal origin that contain various kinds of fatty materials (Table 4). The term “resins” or “lacs” can also be used for plant or insect secretions that take place along resins ducts, often in response to injury or infection, and result in more acidic substances (Hernandez 1994). However, all waxes tend to contain wax esters as major components, i.e., esters of long-chain fatty alcohols with long chain fatty acids. Depending on their source, they may additionally include hydrocarbons, sterol esters, aliphatic aldehydes, primary and secondary alcohols, diols, ketones, triacylglycerols, etc.
Waxes usually present an orthorhombic system of crystallization, favoured by slow cooling rate, and possibly, a small fraction of hexagonal crystals. They possess variable mechanical properties depending of their composition. Carnauba waxes are harder than all the other waxes to which they are added to improve their strength and gloss. Candelilla waxes solidify slowly and reach an intermediate hardness between carnauba and beeswax. Beeswax is relatively flexible and presents a viscoelastic behaviour (Shellhammer, Rumsey and Krochta 1997).


<table>
<thead>
<tr>
<th>Class</th>
<th>Source</th>
<th>Type of waxes</th>
<th>Molecular species prevalent in the composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mineral / Fossil</td>
<td>Petroleum</td>
<td>Paraffin</td>
<td>Mixtures of straight-chain alkanes</td>
</tr>
<tr>
<td></td>
<td>Lignite/brown coal</td>
<td>Polyethylene wax</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Microcrystalline wax</td>
<td></td>
</tr>
<tr>
<td>Animal</td>
<td>Bees secretion</td>
<td>Beeswax</td>
<td>Wax esters (C40 to C46 molecular species)</td>
</tr>
<tr>
<td></td>
<td>Insect secretion</td>
<td>Shellac</td>
<td>Wax esters (C28 to C34)</td>
</tr>
<tr>
<td></td>
<td>Whale tissues</td>
<td>Chinese wax</td>
<td>Wax esters (C46 to C60)</td>
</tr>
<tr>
<td></td>
<td>Collected on sheep wool</td>
<td>Spermaceti</td>
<td>Wax esters (mainly cetyl palmitate-C32 and myristate-C30)</td>
</tr>
<tr>
<td>Botanical</td>
<td>Brazilian palm tree</td>
<td>Carnauba</td>
<td>Wax esters (C18 to C22 fatty acids linked to C20 to C24 fatty alcohols)</td>
</tr>
<tr>
<td></td>
<td>Mexican shrub</td>
<td>Candelilla</td>
<td>Hydrocarbons (C29 to C33), fatty esters</td>
</tr>
<tr>
<td></td>
<td>Jojoba seeds</td>
<td>Jojoba oil</td>
<td>Fatty esters (C38 to C44)</td>
</tr>
<tr>
<td></td>
<td>Rice</td>
<td>Rice bran oil</td>
<td>Unsaponifiable, long chain alcohols (C26 to C30)</td>
</tr>
<tr>
<td></td>
<td>Berries kernel and skin</td>
<td>Japan wax</td>
<td>Palmitic acid triacylglycerols</td>
</tr>
<tr>
<td></td>
<td>Wood pulp</td>
<td>Wood rosin</td>
<td>Variable (hydrocarbons, wax esters)</td>
</tr>
<tr>
<td></td>
<td>Multiple others</td>
<td>Apple, bamboo, sugar cane, citrus fruits...</td>
<td></td>
</tr>
</tbody>
</table>
Wax coatings have been used since the 1930s to control desiccation and ripening of fresh fruits and vegetables by limiting gas diffusion (Callegarin et al. 1997; Hernandez 1994; Kester and Fennema 1986). Such coatings also reduce the surface abrasion of the fruit surface during handling, improve appearance by enhancing surface gloss and were used as carrier for other active components such as fungicides. However, if the gas permeability of the coating is not adequate, waxing can result in the creation of a modified internal anaerobic atmosphere inducing off-flavours and deterioration of the product (Baldwin et al. 1997). Many wax coatings are applied as emulsions (macro-emulsions particles size range 2,000-100, 000 Å or micro-emulsions particles size range 1,000-2, 000 Å) or as wax suspensions. Though most natural waxes have emulsifying properties, the stability of the wax emulsion is reinforced by the use of surface active agents such as fatty acids (palmitic, oleic, stearic etc), glycerol and fatty acids derivatives or lecithins (Hernandez, 1994). Numerous applications of wax coatings on whole citrus fruits have been reported in the scientific literature: emulsion candelilla wax/water on limes (Paredes, Camargor and Gallardo 1974), carnauba wax on lemons (Hagenmaier and Baker 1994; Hagenmaier and Baker 1995). Wax coatings have also been applied on slightly processed fruits: carnauba wax on grapefruit pieces (Hagenmaier and Baker 1997), beeswax on orange fruits (Baldwin et al. 1997), other wax coatings on apples and pears (Drake and Nelson 1990; Drake and Nelson 1991), peaches (Kraght 1966), tropical fruits and vegetables (Baldwin 1994; Baldwin, Burns, Kazokas, Brecht, Hagenmaier, Bender and Pesis 1999; Hoa, Ducamp, Lebrun and Baldwin 2002; McGuire 1997). A limited number of processed food products have also been coated with waxes and lacs, such as shellac: waxing of candies and breakfast cereal mixes (Lowe, Durkee, Hamilton and Morgan 1963; Bolin 1976; Seaborne and Egberg 1989), application of commercial glazing and anti-sticking blends (waxes/lacs alcoholic dispersions or suspensions) on confectionery and dry fruits (Capol®, Kaul GmbH, Germany). The restricted use of waxes and lacs as edible coatings for processed food products can be explained first by regulatory concerns and secondly because of their high melting point responsible for unappealing sensorial properties (hardness and waxy residues).
Table 5. Summary of the U.S Code of Federal Regulations (Title 21, Food and Drug Administration) and directive 95/2/EC concerning the use of the main kinds lipid film-forming materials different from waxes, lacs and their derivatives, as coating or components of coatings in food products (Anonymous 1977; Anonymous 2004b).

<table>
<thead>
<tr>
<th>Substances</th>
<th>Authorized applications in the U.S Code of Federal Regulations [CFR section]</th>
<th>Authorized applications in the consolidated directive 95/2/EC [E No]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fatty acids</td>
<td>Lubricant, binder, and defoaming agent; Limit: GMP*; [172.860]</td>
<td>#: Limit: quantum satis**; [E 570]</td>
</tr>
<tr>
<td></td>
<td>Stearic acid: GRAS*** substance; Limit: GMP; [184.109]</td>
<td></td>
</tr>
<tr>
<td>Mono and diglycerides</td>
<td>GRAS substance; Limit: GMP; [184.150]</td>
<td>#: Limit: quantum satis; [E 471]</td>
</tr>
<tr>
<td>Acetylated glycerides</td>
<td>Monoglycerides, multipurpose additive; Limit: quantum satis; [172.828]</td>
<td></td>
</tr>
<tr>
<td>Lactic acid esters of mono and diglycerides</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acetylated or none Tartaric Acid Esters of Mono and Diglycerides (DATEM)</td>
<td>DATEM, GRAS substance; Limit: GMP; [184.1101]</td>
<td>#: Mono and diacetylated DATEM [472 e]; DTEM [472 d]; mixed acetic and tartaric acid esters of mono and diglycerides [E 472 f]; Limit: quantum satis</td>
</tr>
<tr>
<td>Sucrose fatty esters</td>
<td>Emulsifiers or stabilizers in various goods; texturizers in various goods; components of protective coatings applied to a restricted number of fruits to retard ripening and spoiling; Limit: GMP; [172.859]</td>
<td>Colours and fat soluble antioxidant; [E 473]</td>
</tr>
<tr>
<td>Polyglycerol esters of fatty acids</td>
<td>Cloud inhibitor in vegetable and salad oils, emulsifiers in dry or whipped topping base; [172.854]</td>
<td>Fine bakery, granola breakfast (10 g/kg), emulsified liqueur (5 g/l), egg products (1g/kg), beverage whiteners (0.5g/kg), chewing gum, fat emulsions, milk and cream analogues (5 g/kg); sugar confectionery, desserts (2 g/kg); [E 475]</td>
</tr>
<tr>
<td>Salts of fatty acids</td>
<td>Binder, emulsifier, and anticaking agent in food; Limit: GMP; [172.863]</td>
<td>#: Sodium, potassium and calcium salts of fatty acids; [E 470 a]; magnesium salts of fatty acids; [E 470 b]; Limit: quantum satis</td>
</tr>
<tr>
<td>Lecithins</td>
<td>GRAS substance; Limit: GMP; [184.1400]</td>
<td>#: Limit: quantum satis; [E 322]</td>
</tr>
</tbody>
</table>

* GMP: Good Manufacturing Practices;  
**Quantum satis: Amount not to exceed that required to produce the intended effect;  
***GRAS: Generally Recognized As Safe for human consumption;  
#: Additives which may be added to all foodstuffs except for those referred to in the Article 2 (3) of the consolidated directive 95/2/EC.
In the classification of moisture barriers efficiency established by Kester and Fennema, waxes are followed by stearyl alcohol, acetyl acyl glycerols, hexatriacontane, tristearin and stearic acid (Kester and Fennema 1989a). These authors observed that stearic alcohol was seven times more impervious to water transfer (0-100 % RH gradient) than stearic acid. This result can be explained by the lower polarity of the hydroxyl function compared to the carbonyl function but also to the specific sheet structure developed by the stearyl alcohols. Fatty alcohols and fatty acids lack structural integrity to form strong continuous coatings and are used mainly as emulsifying or dispersing agents in combination with other biopolymers. The formulation of multi-component films can affect their properties. McHugh and Krochta (Gennadios et al., 1994) observed that composite films based on fatty alcohols/whey proteins were less effective as moisture barriers than fatty acids/whey proteins. This discrepancy with Kester and Fennema’s study could be explained by the influence of the polar support of the fatty alcohol composite film on moisture transfer.

Roth and Longin (1984) showed that C16 or C18 fatty alcohols were the most effective to limit water evaporation from the surface of hydrated products. Similarly, Hagenmaier and Baker (1997) reported that micro-wax emulsions including stearic and palmitic acids were more effective to limit fruit desiccation than those using lauric and oleic acids as emulsifiers. Koelsch and Labuza (1992) showed that the moisture barrier properties of composite films (emulsions: methylcellulose/ fatty acids, 70:30) increased with the degree of saturation and fatty acid chain length up to 18 carbons. The higher efficiency of stearic and palmitic fatty acids and alcohols compared to component of similar chemical nature but of different chain length was reported in various other studies (Hagenmaier and Shaw 1990; McHugh and Krochta 1994c; Park, Testin, Park, Vergano and Weller 1994). The positive effect of long aliphatic chain up to 18 carbons could be explained by an increased apolar part in the molecule which does not favour water solubility in the film. Above this threshold, the aliphatic long chains induce a more heterogeneous structure.

Similarly to fatty acids and fatty alcohols, acyl glycerols (esters of glycerol and fatty acids) are often used as emulsifying and dispersing agents because of their poor mechanical properties (Table 5). Higuchi and Aguiar (1959) could not investigate the moisture barrier properties of pure self-supported films of di- and tri-glycerol stearates, because of the development of structural defects. However they studied pure glyceryl-monostearate film and blends of glyceryl-stearate with beeswax. The resistance to water transfer of glyceryl-monostearate appeared highly dependent on the relative humidity gradient the film was subjected to. This conclusion was in agreement with another study dealing with a monostearil-glycerol film formed on a cellophane support (Martin-Polo and Voilley 1990). The film showed moisture barrier properties ten times higher than cellulose triacetate and cellulose acetate propi-
onate films but much lower than synthetic plastic films. Mono-stearyl glycerol has been reported as a very effective emulsifier to improve the adherence of an alcane layer on a hydrophile suppprt (Quezada Gallo et al. 2000). In the classification of lipid materials established by Kester and Fennema (1989a), tristearyl-glycerols were reported as 1.5 times more resistant to water transfer than stearic acid but half as resistant as hexatriacontane (alcane).

Acetyl-acyl-glycerols (acyl glycerols with 1 or 2 acetyl group on the glycerol molecule) commonly called acetylated glycerides, can be prepared through a reaction between glycerides and acetic anhydride or through a catalysed interesterification of edible fats with triacetin. A highly noticeable property of these compounds compared to other lipids is a good flexibility in their $\alpha$-polymorphic form. The acetylated glycerides are also characterized by a high resistance to oxidative degradation, a non greasy touch and a low melting point resulting from the presence of acetyl groups in the glyceride molecule. Used at concentration from 2 to 10 % (w.b.), they make excellent plasticizers and significantly improve the mechanical properties of high melting point fats or of other fats at low temperature (Alfinslater, Coleman, Feuge and Altschul 1958). Their properties depend on the nature of the acyl-glycerols they are based on, and on their acetylation degree. For example, aceto-stearin films have oxidative stability, especially if derived from hydrogenated vegetable oils, while aceto-olein films are less resistant to oxidation. Tailored functional properties of blends can thus be achieved by combining various molecules (Alfin-Slater 1958; Feuge et al. 1953). Distilled acetylated monoglycerides coatings produced under the trade name Myvacet (Eastman Chemical Product., Kingsport, TN) were first used in edible packaging application on fresh products in the late 1950s (Woodmansee and Abbott 1958). Scientific and patent literature disclose numerous examples of application on meats (Dawson, Zabik and Sobel 1962; Schneide 1972; Stemmler and Stemmler 1974; Zabik and Dawson 1963), frozen fish (Hirasa 1991; Stuchell and Krochta 1995), fresh or dry fruits, and vegetables (AvenaBustillos, Krochta and Saltveit 1997; Mate and Krochta 1997)

More recently water-related properties and water barrier properties of acetylated monoglycerides and diglycerides presenting variable chain length and acetylation degrees were evaluated by Guillard et al. (2003). The extension of shelf-life enabled by such films in a two-component composite bakery food product (sponge-cake/ barrier film/ agar gel) was estimated. Films with the highest acetylation degree (70%) presented significantly lower moisture sorption on the high $a_w$ range (0.70-1.00), than other compounds and enabled the best extension of the baked product shelf-life. This observation was in accordance with the decrease in HLB (hydrophilic-lipophilic balance) observed between not acetylated (glycerol monostearate, H.L.B. of 3.8) and acetylated monoglycerides (H.L.B. of 1.5) (Hernandez, 1994). According to model predictions, the most effective barrier (100 µm thick) delayed
for more than 20 days the increase of the sponge-cake moisture content from 23 to 40% (w. b.) which was reached in less than 2 days in the product without barrier. Few applications and sensory problems associated with acetylated glycerides edible coatings have been reported, including the tendency of coatings from highly saturated acetylated compounds to crack and flake during refrigerated storage (Hirasa 1991), to pick up foreign flavours (Zabik and Dawson 1963), and to exhibit acidic or bitter aftertaste attributed to acetylated compounds (Morgan 1971). Because of their fluidity, oils exhibit poor moisture barrier properties that can nevertheless be improved by hydrogenation. They are widely used in refrigerated or frozen product, possibly after a winterization (removal of crystalline triacylglycerols).

Among the list of the numerous materials that can be used as moisture barriers, cocoa butters and cocoa-based films are the most widely used in the confectionery (chocolate) and bakery industries (Biquet and Labuza 1988; Morillon et al. 2002). The good sensorial properties of chocolate permit using thick perceptible coatings that will both resist moisture migration and increase the commercial value of the product. The first comprehensive study on chocolate barrier property was done by Biquet and Labuza (1988). These authors determined the moisture sorption isotherms, effective diffusion coefficient and water vapour permeability of a dark chocolate film (0.6 to 1.2 mm thick). They reported that a 0.6 mm coating of semi-sweet dark chocolate used as barrier coating on a monocomponent system (agar gel) was a more effective moisture barrier than a 0.025 mm low density polyethylene coating. However, Guillard et al. (2003) pointed out the poor water barrier properties of dark chocolate film used at the interface between two components in the high a_w range (a_w > 0.8) which could be explained by sugar dissolution phenomena. A comprehensive review and several publications on the barrier properties of chocolate were recently published by Gosh (Ghosh et al. 2002; Ghosh 2003; Ghosh, Duda, Ziegler and Anantheswaran 2004; Ghosh, Ziegler and Anantheswaran 2005).

3 Formulation and structuring of moisture barrier films

Plasticizer addition and combination of materials (lipids, hydrocolloids or blends of lipids and hydrocolloids) are usually used to formulate moisture barriers and overcome the problems associated with the use of a single film-forming material.

3.1 Addition of plasticizer

The cohesiveness and flexibility of edible films are determined by the molecular weight, branching and polarity of their constituents. Molecules with low polarity and high linearity tend to produce films with high degree of cohesiveness and rigidity
Plasticizers, by weakening intermolecular forces between adjacent polymer chains, reduce brittleness, increase flexibility and tear resistance of edible films. This is particularly important when the product is stored at a low RH and/or temperature. The plasticizer must be compatible (miscible) with the polymer and if possible with its solvent. Plasticizers having food applications include: (a) mono-, di-, oligo-saccharides (mainly glucose and fructose-glucose syrups, honey), (b) polyols (mainly sorbitol, glycerol, glyceryl derivatives and polyethylene glycols), (c) lipids and derivatives (mainly fatty acids, monoglycerides and ester derivatives, phospholipids, surfactants). The formulation of films including plasticizers (usually added from 10 to 30 % d.b.) must be conducted carefully, since they tend to migrate, diluting and softening the structure of the film, resulting in lower water resistance (Guilbert 1986).

3.2 Combination of different fat materials

Multilayered pure fat structures were advocated in several patents (Nielsen, Sparso and Kristiansen 2001; Van Gastel 2006). Recently a bilayered barrier which combined a soft spreadable fat (oil continuous spread, Solid fat content of 5-20 % at 20°C) and a high (> 35°C) melting point fat has been patented (Van Gastel 2006). The soft spread fills up the pores and homogenises the product surface whereas the second layers confers the moisture resistance. Another multilayered lipid-based barrier has been recently patented too (Gaonkar and Herbst 2004; Gaonkar and Chen 2005; Loh and Hansen 2002; Smith and Almendarez 2004). It includes a flexible layer (50 µm to 1 mm thick) containing short chain fatty acids crystallized in the α-form and a moisture resistant hydrophobic layer composed of a low melting fat (< 35°C) in which have been dispersed micro-particulated high-melting point fat (MP> 70°C). The microparticules can be added up to 35% (w.b.) of the hydrophobic layer and are responsible for fat crystals control and stabilization.

3.3 Combination of hydrocolloids

Numerous examples of polysaccharide-protein, polysaccharide-polysaccharide, protein-protein multi-components films have been available since the 1990s. Synergic effects between components, which result from interactions between the macromolecules, such as charge-charge electrostatic linkage, hydrogen bonding and covalent cross-linking have been researched. The resulting multi-components edible barriers can show improved water transfer resistance. For example, film barrier properties are improved by substituting 30 % of gluten by keratin (Gennadios, Weller and Testing 1993), by incorporating non-fat dry milk to acidic polysaccharide films such as alginate and pectin films (Parris, Coffin, Joubran and Ressen 1995) and in microcrystal-
Multi-components films may additionally present improved flexibility (García, Pinotti, Martino and Zaritzky 2004; Lazaridou and Biliaderis 2002; Park, Lee, Jung and Park 2001) and sensorial properties (Longares et al. 2005).

### 3.4 Composite films

Pure lipids can be combined with hydrocolloids such as proteins, starches or celluloses and their derivatives, either by incorporating the lipids in the hydrocolloid film-forming solution (emulsion technique) or by depositing the lipid layer onto the surface of the pre-formed hydrocolloid film to obtain a bilayer (Fennema and Kamper 1986; Krochta and De Mulder Johnston 1997). Multi-components films have been extensively reviewed by Wu et al. (2002). The addition of non lipid-compounds (hydrocolloids, sugar solids…) as dispersed components in fat materials permits forming fat dispersions (e.g. chocolate, Fig. 2).

These composite films take advantage of the distinct functional properties of each class of film-formers: the moisture barrier properties of lipids and the ability to form a resistant matrix of the hydrocolloids. The resulting water barrier efficiency of bilayered films is often of the same order of magnitude than that of pure lipid (Debeaufort, Quezada-Gallo, Delporte and Voilley 2000c) and is much higher than that of emulsion-based films (Debeaufort and Voilley 1995; Debeaufort, Martin-Polo and Voilley 1993; Martin-Polo, Mauguin and Voilley 1992; McHugh and Krochta 1994a; McHugh and Krochta 1994b). There are, however, a number of drawbacks associated with bilayered moisture barriers. The hydrocolloid layer is hydrophilic and tends to absorb water especially when the film is in direct contact with high water activity foods (> 0.75). Furthermore, the additional processing steps (casting and drying) required to form these films, make them difficult to use in high speed commercial production.
With regard to polysaccharide-lipid films, the most cited in literature are cellulose ether-based, mainly MC and HPMC-based films. Though other trials with pectinate, chitosan, starch, alginate have also been done. The interest towards cellulose derivatives can be explained by their excellent film-forming properties. Composite emulsified films based on HPMC/MC, stearic acid or palmitic/stearic acids blend, and possibly covered by a beeswax layer (Kamper and Fennema 1984a; Kamper and Fennema 1984b; Kamper and Fennema 1985; Rico-Pena and Torres 1990), but also bilayers of Methylcellulose/waxes (Greener and Fennema 1989a; Greener and Fennema 1989b), presented really good moisture barrier properties and were early patented (Fennema and Kamper 1986). Starch/alginate/lecithin/stearic acid emulsified
film, tested by Wu et al. (2001) on a 50-100 % RH difference also presented high water barrier resistance.

The possible associations of proteins and lipids in edible films have also been explored but less intensively than for polysaccharides (Wu et al. 2002). Their moisture barrier performance is generally lower than that of composite polysaccharide/lipid-based films. Among all the combinations tested and reported in scientific literature, the best moisture barrier properties were attributed to wheat gluten/lipid films (more precisely beeswax/wheat gluten/glycerol/diacetyl tartaric ester of monoglycerides; Gontard, Duchez, Cuq and Guilbert 1994) and soy protein isolate/lipid films (more precisely soy protein isolate/glycerol/lecithin/stearic acid; Rhum et al. 1999). A moisture barrier based on a prolamin (10-90%), in combination with a lipid (oil preferably: 0.1 to 50 %) and the salt of a fatty acid has been recently patented (Plijterschuddemat, Plijter, Van Son, Ilhelmus, Don and Noort 2003). The resulting coating combines high mechanical strength, improved moisture barrier property and heat stability. Combination of shellac with prolamins presents similar properties (Glasser 1983).

3.5 Addition of non-lipid compounds as dispersed components

The addition of non lipid fillers or bulking agents to improve the functional properties of edible moisture barrier (viscosity, adherence on substrate) is more frequent in commercial and patented coatings/films than in scientific literature. Indeed, in commercial references the barriers are often tested on the product to protect. Formulations are thus developed to try to adjust the viscosity of the coating and its mechanical properties in order to obtain a good adherence and protection to the coated product. Conversely, in scientific articles, barriers have been most of the time evaluated as independent self-supported films.

The addition of dispersed saccharides/polysaccharides to enhance the adherence of composite or fat coatings on bakery product has been suggested in various patents (Anonymous 1979; Haynes, Zhou, Slade, Levine and Chan 2004; Heuvel, Lewis and Povey 1997; Youcheff, Wodke and Perkins 1996). The effect of sugars, cocoa powder, emulsifier and fat type on the WVP (3.5-100 % RH, 20°C) of chocolate coatings was investigated by Gosh et al. (2005) and underlined the favourable effect of sucrose on the WVP of the barrier.

The addition of inert filler material in a fat coating or a modified fat coating have been proposed in several patents (Bastiaans and Tap 2005; Rubenstein and Bank 1982; Rubenstein and Pelaye 1986). Inert fillers increase the viscosity of the fat in the molten state and evidently change its physical properties and enhance the water-occluding action, possibly by improving the coating flexibility and its resistance to external stresses. Inert filler materials must not be chemically reactive,
therewith, not too hygroscopic, mechanically dispersible and possess a particle size such that they do not adversely affect the smoothness and sensorial properties of the coating. Typical filler materials include starches, chemically modified starches, dextrins, microcrystalline cellulose and insoluble cellulose derivatives but also inorganic compounds such as food grade talc, titanium dioxide, silicon dioxide, single silicates, clay materials, insoluble carbonates and phosphates. The amount of the filler material (10-25 % w/w of the coating) also depends upon the particular type of filler utilized. If the use of inert fillers such as starch or dextrin in a fat layers improves its mechanical property and facilitate the coating application (application on ice cream cone; Rubenstein and Pelaez 1986), inorganic fillers, such as silicates, improve the moisture resistance of the barrier. Such coating permits protecting moisture sensitive food ingredients such as crispy cereals to retain their crispness even in a chilled but not frozen environment for a prolonged period, i.e. four weeks or more (Bastiaans and Tap 2005).

4 Coatings application techniques and critical points

4.1 Selection of the techniques of application

Thermoplastic processes used to form edible films and coatings are adapted from techniques developed for synthetic polymers but take into account the specificities of natural polymers (sensibility to heat, chemical or mechanic treatment, high viscosity). These processes include: extrusion (Naga, Kirihara, Tokugawa, Tsuda and Hiototsuka 1996), injection-moulding, extrusion-blowing (Fishman, Coffin, Konstance and Onwulata 2000; Liu, Kerry and Kerry 2006; Psomiadou et al. 1996; Sotthornvit, Olsen, McHugh and Krochta, 2007) and compression-moulding (Cunningham, Ogale, Dawson and Acton 2000).

Thermoplastic processes are attractive since they avoid the need to add and remove solvent but have not been as much explored as the applications from a solution or dispersion of the film forming material. The trials of extrusion, injection-moulding, compression-moulding with biopolymers and more specifically with oilseed proteins - soya (Choi, Lee and Park 2006; Foulk and Bunn 2001), sunflower (Orliac, Rouilly, Silvestre and Rigal 2002; Orliac, Rouilly, Silvestre and Rigal 2003) - and starches (Arvanitoyannis, Biliaderis, Ogawa and Kawasaki 1998; Fang, Fowler, Escrig, Gonzalez, Costa and Chamudis 2005; Fishman et al. 2000; Psomiadou, Arvanitoyannis, Biliaderis, Ogawa and Kawasaki 1997; Suknark, Phillips and Chinnan 1997) targeted biodegradable plastics packaging. They offered strong tensile strength and included non food-grade products in their composition.

The solutions or dispersions obtained by the ‘solvent’ method can be cast and dry on a flat surface from which they are removed as sheets of material. This technique is
the most widely used in laboratories to test the properties of the films. It can also be used by industries (MonoSol Rx®, Indiana, USA) and preformed moisture barrier films obtained by casting were early patented by Kamper and Fennema (1986). The coating-forming solutions or dispersions are nevertheless more frequently applied directly on the product surface. The techniques of application have been reviewed by Grants et Burns (1994) and include: spraying and spray-coating (drying, cooling and chilling), dipping and draining, falling film, fluidized bed processing, turbines (Table 6).

The dipping method is well adapted to multiple steps applications and to food products that present an irregular surface. After dipping, excess coating is allowed to drain from the product and is then dried or let solidify (Greener Donhowe and Fennema 1994). The thickness of the layer is determined by the viscosity of the coating material and/or by the rate at which the viscosity changes after application. It is widely used in the confectionery industry along with pan coating. This alternative is carried out with the aid of a sugar-coating mill. A smooth, regular and closed surface of coating material is obtained by mutual rotation of centres, on which several layers of coating have been applied. Spraying, unlike dipping, is more suitable for applying a film to only one side of the food to be covered. This is desirable when protection is needed on only one surface, for instance when a pizza crust is exposed to a moist sauce. Air-atomization, which is a common method of micro-encapsulation, can also be considered as a coating technique. It consists in dividing an emulsion of the film-forming material and the material to coat into small drops and dry them in a warm air flow.

The coating systems that can be used to coat an inorganic material on the surface of edible products have been adapted from the biomedical and electronics fields. They include: (a) sputtering or analogous thermal sublimation, (b) electron beam, and (c) plasma deposition but their application in the food industry is still marginal.
Table 6. Techniques of application of edible moisture barriers films depending on the systems characteristics (shape of product to be coated and targeted thickness of the barrier) and their critical points.

<table>
<thead>
<tr>
<th>Substrate shape/characteristics</th>
<th>Flat or with flat surfaces</th>
<th>Irregular</th>
<th>Spherical</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Thin</strong></td>
<td>Brushing: substrate with flat and smooth surfaces, brush rigidity, continuous process, drying stage following application</td>
<td>Fluidized thermoregulated air bed: low density small size particle/ heat resistant, batch process, limited weight of centres, sensibility to heat.</td>
<td>Screw coating: flexibility on substrate shape/ quite resistant, continuous process</td>
</tr>
<tr>
<td><strong>Thin to Thick</strong></td>
<td>Spraying: flat system unless associated to other technologies, continuous process viscosity the barrier at the temperature of spraying, tempering of the barrier, pressurization and nozzle pattern, target thickness</td>
<td>Dipping: Flexibility on substrate shape/ smooth surface of substrate, viscosity of the barrier, adhesion, cooling rate</td>
<td></td>
</tr>
<tr>
<td><strong>Thick</strong></td>
<td>Casing: large samples (e.g. confectionery bars), contraction of the barrier, cooling rate and temperature control</td>
<td>Pan and Drum coating: spherical substrate/ quite resistant, hard shelf on soft product (sugars coatings on jelly beans/candied fruit), batch process, heat balance control, adhesion, avoid cluster formation</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Enrobing: Flexibility on substrate shape/ maximal temperature of the falling film, viscosity, temperature balance substrate/barrier</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Coextrusion: cold flow of the filling, minimal thickness of barrier wall (1 mm), barrier formulation, splitting of the rope</td>
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</tbody>
</table>
4.2 Critical factors to consider in barrier coating development

Many known barrier coatings suffer from the disadvantage that they are difficult to apply. Furthermore, to be effective, they are often applied in a thick layer which reinforces their detrimental effect on taste and texture. The difficulty in their application can arise from the product itself: very irregular or porous surfaces make the control of the barrier thickness difficult resulting in poor ineffective coatings with defects. When lipids are used, they can impart a waxy or gummy mouth feel. Hence, the sensorial properties of the barrier have to be taken into account since they may interfere with the product characteristics. Surprisingly however, research on the sensory properties of edible film has been limited (Kim and Ustunol 2001; Longares, Monahan, O’Riordan and O’Sullivan 2004).

The compatibility and resulting adherence between the food surface and the coating can be critical. It is generally the case when a hydrophobic material is used to protect a hydrophilic product. A surface active agent or other kind of material (starch or cocoa powder) compatible with the two products can help improving the coating adherence (Nussinovitch 1998). Most application techniques involve a drying or a solidifying stage of the coating after its application. This stage is critical in the process since it influences the adherence of the coating to the product and its thickness. On the other hand, for economic reasons this stage has to be as short as possible. The parameters of the drying or solidification stage (temperature, air flow, etc), but also the temperature and the state of the receiving surface have to be strictly controlled to avoid irregular coating formation.

In addition, the coating has to resist to the conditions of storage and of preparation of the food product, e.g. storage temperature, oven or microwave heating. Many ready-to-eat composite food products to which edible moisture barriers are applied are intended to be heated before consumption. Common lipid-based coatings tend to melt and flow under normal baking conditions and, thus, loose film integrity and barrier effectiveness. On the other hand, composite coatings can include temperature sensitive compounds, such as proteins that may be denaturated by heat, and result in drastic modifications of the barrier properties. Edible moisture coatings specifically formulated to resist elevated temperature or specific processes, such as microwave heating, have been developed and are disclosed in the patent literature. Regarding microwave heating, complex coatings have been proposed: a bilayer comprising first an hydrophilic layer (dough layer, methylcellulose, carrageenan) which includes a susceptor (glycerine, sucrose ester, and chloride salt) and then a moisture resistant layer (Simon, Sheen and Moyer 1995). This coating allows producing and stabilizing a food with a crisp exterior and a soft, tender interior. Davis and Gibbs (1991) proposed using a barrier coating (comprising fats and a milk protein) in chilled compos-
ite products which are to be eaten hot. The coating softens on heating without phase separation, is compatible with the product both visually and organoleptically, and results in an extended shelf-life.

5 Conclusions and future trends

An extremely wide range of edible moisture barriers has been explored in the scientific and patent literature since the 1950s. The use of such barriers on fresh and slightly modified fruits and vegetables, meats, fish and seafood, mimicking or complementing naturally present protective layers, is now generalized. The combination of various types of film-forming agents (polysaccharides, proteins, lipids) along with the improvement in the film forming methods, the possible modifications of the film-forming materials (denaturation, cross-linking, acetylation, grafting, etc) has allowed the improvement and tailoring of the water vapour resistance of some barrier films. The necessity of adopting an integrated approach in the development of edible moisture barriers to combine regulatory, nutritional, organoleptic and technical requirements (Fig. 3) is well illustrated in the recent patent literature. Indeed, most of the patents not only disclosed the barrier composition but also the food product in which it has to be applied and the technique of application of the barrier. This integrative approach should also be adopted in the scientific papers dealing with the determination of moisture barriers efficiency, to determine accurately the promises of a specific barrier in a given food product.

The field of multidomain ready-to-eat food products is still developing and remains nowadays the more challenging in terms of moisture transfer control. Edible moisture barriers appear as an interesting answer to consumers’ demand for composite product with good nutritional value and stable organoleptic properties. However, the development of coatings including inorganic compounds seems to be a new trend, interesting to reinforce the barrier property of the film but which may not be well accepted by the consumers. Hence, the necessity of developing and characterizing, simply formulated, flexible, easy to apply moisture resistant barriers is still of prime importance. These edible moisture barriers are all the more attractive as they could limit the use of highly water-resistant multilayered synthetic packaging film, generally non-recyclable.
Fig. 3. Promises and limits of edible moisture barriers.
References


Baldwin, E. A., Burns, J. K., Kazokas, W., Brecht, J. K., Hagenmaier, R. D., Bender, R. J. and Pesis, E. (1999) Effect of two edible coatings with different permeability characteris-


Edible moisture barriers


Edible moisture barriers


Edible moisture barriers