Critical Reviews in Food Science and Nutrition

Edible Moisture Barriers: How to Assess of their Potential and Limits in Food Products Shelf-Life Extension?

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Published online: 27 Apr 2009.

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Edible Moisture Barriers: How to Assess of their Potential and Limits in Food Products Shelf-Life Extension?

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Control of moisture transfer inside composite food products or between food and its environment remains today a major challenge in food preservation. A wide rage of film-forming compounds is now available and facilitates tailoring moisture barriers with optimized functional properties. Despite these huge potentials, a realistic assessment of the film or coating efficacy is still critical. Due to nonlinear water sorption isotherms, water-dependent diffusivities, and variations of physical state, modelling transport phenomena through edible barriers is complex. Water vapor permeability can hardly be considered as an inherent property of films and only gives a relative indication of the barrier efficacy. The formal or mechanistic models reported in literature that describe the influence of testing conditions on the barrier properties of edible films are reviewed and discussed. Most of these models have been validated on a narrow range of conditions. Conversely, few original predictive models based on Fick's Second Law have been developed to assess shelf-life extension of food products including barriers. These models, assuming complex and realistic hypothesis, have been validated in various model foods. The development of nondestructive methods of moisture content measurement should speed up model validation and allow a better comprehension of moisture transfer through edible films.

Keywords Moisture transfer, lipid, water vapour permeability, modelling

INTRODUCTION

Protective moisture barriers can be found on many plants and other living organisms especially those subject to high variations in environmental conditions or long dry spells. Many uses of edible coatings are based on the imitation of these natural functions. Edible protective films or coatings have been generally defined as thin layers of material which are eaten by the consumer and provide a barrier to mass transfer (moisture, oxygen, and 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 (Guilbert, 1986; Shellhammer

and Krochta, 1997a). Moisture barriers uses gather extremely old practices such as fruit waxing used in the XII century in China, or meat larding used in England during the 16th century (Kester and Fennema, 1986) but still remains today an important tool to maintain the quality of slightly modified (fruits, fruit pieces) or processed products (Debeaufort et al., 2002; Guilbert et al., 1996; Guillard et al., 2003; Koelsch, 1994). Edible coatings provide specifically attractive solutions to retard moisture transport within composite food products, i.e. food in which distinct water activity (a_w) components are put into contact and in which synthetic packaging can not be included.

Due to their low affinity with water, lipids are generally considered as the most effective moisture barrier and are included in protective coating formulation. Lipid-based materials presenting poor mechanical properties are frequently improved by association with proteins and/or polysaccharides (Wu et al., 2002). Conversely, due to their hydrophilic nature, pure polysaccharide and protein films exhibit limited water vapor barrier ability.

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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). Pure, thin, amorphous inorganic coatings have lately been presented as effective moisture barrier-forming materials in patents literature (Bastiaans and Tap, 2005; Beyer et al., 1996).

Several reviews focusing specifically on edible moisture barriers (Bourlieu et al., In press; Debeaufort et al., 2000a; Debeaufort et al., 2002; Koelsch, 1994) and/ or lipid-based edible films have been published (Baldwin et al., 1997; Callegarin et al., 1997; Greener and Fennema, 1992; Hernandez, 1994; Morillon et al., 2002; Shellhammer and Krochta, 1997a). The necessity of dealing concurrently with regulatory, nutritional, organoleptic, and technical requirements to develop effective moisture barriers was underlined in these reviews. However, assessment of moisture barriers efficacy is often reduced to film Water Vapor Permeability (WVP) measurements and to the analysis of the material physical properties. Barrier properties have been scarcely studied in situ, i.e. in a real or model food product. The target of the present review is to assess moisture barriers promises and limits to extend food shelf-life confronting classical barrier properties and more recent modelling approaches. After a presentation of the wide range of film-forming materials now available, the discussion will focus on the assessment of the moisture barrier properties of the films and their critical points. Examples of prediction of moisture barrier efficacy in model food products will then be presented.

A WIDE RANGE OF FILM-FORMING MATERIALS AND POSSIBILITIES FOR STRUCTURING THEM

Usual Film Forming Materials

A wide range of hydrophobic compounds can be used in the formulation of moisture barriers and have been examined since the 30s (Morillon et al., 2002). Edible waxes and lacs are widespread protective barriers in nature and currently serve as barrier-forming materials. The term "wax" is used for a variety of products having four major sources (mineral, botanical, animal, and synthetic) but without any satisfactory chemical definition (Table 1). The terms "resins" or "lacs" can also be used for more acidic substances secreted by plants or insects (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 the source of the waxy material, they may additionally include hydrocarbons, sterol esters, aliphatic aldehydes, primary and secondary alcohols, diols, ketones, triacylglycerols and the like. Waxes and lacs are highly resistant to biodegradation, practically indigestible, and not metabolized when orally ingested by humans and animals. They possess variable mechanical properties depending on their composition and therefore, their melting range.

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 visco-elastic behavior (Shellhammer et al., 1997b).

Wax and lac coatings have been used since the 1930s to control the desiccation of fresh fruits and vegetables and their ripening through gas diffusion limitation (Callegarin et al., 1997; Hernandez, 1994; Kester and Fennema, 1986). Waxing is performed in part to replace the natural waxes that picked up contaminants and are removed by washing. Wax coatings also reduce the surface abrasion of the fruit during handling, improve appearance by enhancing surface gloss, and are often used as carrier for other active components such as fungicides. However, waxing can result in the creation of a modified internal anaerobic atmosphere inducing off-flavors and deterioration of the product (Baldwin et al., 1997). A limited number of processed food products has also been coated with waxes and lacs. These applications gather waxing of candies and breakfast cereal mixes (Bolin, 1976; Lowe et al., 1963; Seaborne and Egberg, 1989), application of commercial glazing and anti-sticking blends (waxes/lacs alcoholic dispersions or suspensions) on confectionery and dry fruits, application of emulsions on fresh cut fruits, and fish meat (Gogus et al., 2006; Perez-Gago et al., 2003).

The other major group of lipid coatings consists of fatty acids and their glycerides (Shellhammer and Krochta, 1997a; Shellhammer and Krochta, 1997c). Whatever the melting point of such compounds, their moisture barrier properties are limited. High melting point ($>35°C$) compounds, lack structural integrity to form strong continuous coatings and are used mainly as emulsifying or dispersing agents in combination with other biopolymers. Low melting point compounds and oils (gathering triglycerides with variable chain lengths) present poor moisture barrier properties due to low Solid Fat Content (see Section titled Modelling Film Moisture Barrier taking into a account interactions with Moisture). They are widely used in refrigerated or frozen products, possibly after a winterization. Hydrogenated oils enter in the composition of several commercial moisture barriers (Table 2).

Of particular interest as coatings, acetyl-acyl-glycerols commonly called acetylated glycerides can not be extracted from natural resources and are produced by chemical synthesis. A really noticeable property of these compounds compared to other lipids is their good flexibility. 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 group(s) 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 other fats at low temperature. Their properties depend on the nature of the acyl-glycerols they are based on and on their acetylation degree. Tailored functional properties of blends can thus be achieved by combining various molecules (Alfinslater et al., 1958; Feuge, 1954). Scientific

Table 1 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 of waxes, lacs and their derivatives as coating or components of coatings in food products (Anonymous,1977; Anonymous, 2004)

Sources	Substances	Authorized applications in the U.S. Code of Federal Regulations [CFR citation]	Authorized applications in the consolidated directive 95/2/EC [E No]
Mineral, Fossil or synthetic	Paraffin	Synthetic, protective coating or component of coating for a restricted list of fresh fruits and tubercules (fresh grapefruit, lemons, limes, muskmelons, oranges, sweetpotatoes, and tangerines); Limit: *quantum satis*; [172.275]	(-); #
	Oxidized PE	Protective coating or component of coating for a restricted list of fresh fruits and tubercules and nuts in shell; Limit: GMP*; [172.260]	Surface treatment fresh citrus fruits and melons, papaya, mango and avocado; Limit: *quantum satis*; [E 914] and Montan acid esters [E 912]
	Microcrystalline wax	(−)	Surface treatment of confectionery (excluding chocolate), chewing gum, melons, papaya, mango, and avocado; Limit: *quantum satis*; [E 905]
	White mineral oil	Releasing agent and lubricant (flavoring capsules < 0.6%, bakery product < 0.15%, dehydrated food and vegetables < 0.02%, egg white solids < 0.1%); Protective coating (raw fruits and vegetables, limit: GMP); Hot melt coating (frozen meat < 0.095%); Polishing agent (confectionery <0.2%); Defoamer; [172.878]	(−); #
	Natural and synthetic petroleum wax	Masticating substance (chewing-gum, GMP), protective coating (cheese, fresh fruits and vegetables, GMP), micro-encapsulating agent for spices and flavours; [172.886]; [172.888]	(−); #
Botanical	Rice bran wax	Coating (candy < 50 ppm, restricted list of fresh fruits and vegetables); [172.890]	(−); #
	Wood rosin	Moisture barrier (soft gelatine capsules < 0.07%, ascorbic acid and its salts <7%);	(−); #
	Coumarone Indene resin	Coating component for fresh citrus, limit : 200 ppm fresh fruit weight basis; [172.215]	(−); #
	Carnauba wax	GRAS substance; Anticaking agent, formulation aid, releasing agent, surface agent (GMP in baked goods, chewing gum, confections, frostings, fresh fruits and fruit juices, gravy sauces, processed fruits, soft candies); Limit: GMP; [184.1978]	Glazing agent for confectionery (including chocolate < 500 ppm, chewing gum < 1200 ppm, < 200 ppm for fine bakery products, snacks, nuts, coffee beans, dietary food supplement, and restricted list of fresh fruits, i.e. citrus fruits, melons, apples, pears, peaches and pineapples); Limit: *quantum satis;* [E 903]
	Candellila wax	GRAS substance; Lubricant and surface finishing agent (GMP in chewing gum and hard candy); [184.1976]	Glazing agent and surface treatment for confectionery (including chocolate), fine bakery products, snacks, nuts, coffee beans, dietary food supplement, restricted list of fresh fruits (citrus fruits, melons, apples, pears, peaches, and pineapples); Limit: *quantum satis;* Shellac [E 904], Beeswax [E 901], Candellila wax [E 902]
Animal	Beeswax (white and yellow)	GRAS*** substance; Flavouring agent, adjuvant, lubricant and surface finishing agent (GMP, i.e. in chewing gum <0.065%, <0.05% confections and frostings, <0.04% hard candy, <0.1% soft candy, < 0.002% all other food products); [184.1973]	
	Shellac	Indirect food additive: allowed as component of coating; Limit: GMP; [175.105];[175.300]	

* 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
#: Possible use for food contact of such waxes, lacs and coatings after specific authorization as disclosed in the Framework Regulation (EC) 1935-2004 (L338/4)

Table 2 Examples of commercial lipid-based edible moisture barrier forming materials available on the European market

Type of lipid compound	Commercial name of product	Composition/fat source	Supplier	Target application
Waxes, lacs and derivatives	2442 L, 2442 P100...	Carnauba wax	Kahlwax (Germany)	Polishing agent relasing agent for sweets, chewing gum, coffee, bakery goods, fruits (citrus and other) coating.
	Cera Flava et alba 2039 7302 L 6220	Beeswax Candelilla wax Shellac wax PET wax . . .		
	Michem$^{®}$ Emulsion 62125 AM	Anionic carnauba wax emulsion	Michelman (Belgium)	Fruit coating
Triglycerides	Barrier FAT^{TM}79 and 76	Fractionnated hydrogenated refined vegetable fat of non lauric origin (respective MP:33°C, 37°C)	AarhusKarlsham (The Netherlands)	Coating for bakery goods, composite food, alcohol filled chocolate
	AKOPOL^{TM}, CEBES^{TM}	Cocoa butter replacer/substitute		Non temper compounds: Combination with cocoa liquor, powder, sugar
	ISAO^{TM}43–82 and 43–80	Partially hydrogenated non lauric vegetable fat (MP: 32°C)		Coating for inner side of ice cream cones
	Cotebar^{TM}A, H and M	Fractionated hydrogenated refined vegetable fat of non lauric origin (MP: 45°C)	Loders Croklaan (The Netherlands)	Coating for bakery goods, composite food.
Triglyceride derivatives	GRINDSTED$^{®}$ ACETEM (50–00 P, 70–00 P)	Acetic acid Esters of monoglyceride (acetylation degree: 50 to 70%, MP:35 to 43°C)	DANISCO (Denmark)	Plasticizer, coating for nut, fresh product (meat product,. . .) dry fruits, extend shelf-life and provide moisture barrier
	MYVACET(5–07 K, 7–00, 7-07 K)		Quest Int. (The Netherlands)	
	DIMODAN$^{®}$ / GRINDSTED$^{®}$ MONO-DI	Distilled monoglyceride/ Mono and diglycerides	DANISCO (Denmark)	Antisticking coating, emulsifierand plasticizers
	GRINDSTED$^{®}$ SMS	Sucroesters/sorbitan ester		Control fat crystallization, limit chocolate bloom, emulsifier

and patent literature disclose numerous examples of application on meats (Dawson et al., 1962; Heine et al., 1979; Schneide, 1972; Stemmler and Stemmler, 1974; Zabik and Dawson, 1963), frozen fish (Hirasa, 1991; Stuchell and Krochta, 1995), on fresh or dry fruits and vegetables (AvenaBustillos et al., 1997; Mate and Krochta, 1997) More recently water-related properties and water barrier properties of acetylated monoglycerides and diglycerides presenting variables chain lengths and acetylation degrees were evaluated by Guillard et al. (2003).

Combinations of lipid derivatives as blends or structured multilayers have been advocated in several patents (Nielsen et al., 2001; Van Gastel, 2006). A multilayer which includes a flexible layer (0.05–1 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), was recently proposed (Gaonkar and Chen, 2005; Gaonkar and Herbst, 2004; Loh and hansen, 2002; Smith and Almendarez, 2004). The moisture resistance of the hydrophobic layer is enhanced by the addition of dispersed micro-particles of 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. A simpler bilayered structure which combines a soft spreadable fat (oil continuous spread, solid fat content of 5–20% at 20°C) and a high melting point fat (>35°C) was lately patented (Van Gastel, 2006). The soft fat fills up the pore and homogenizes the product surface whereas the second layer really confers the moisture resistance. A combination of low MP and high (MP >35°C) fats, to obtain an improved flexibility or spreadability from the first, and improved moisture resistance or stabilization from the second, is generally suggested.

Polysaccharides and protein-based films exhibit limited water vapor barrier ability but are applied on short shelf life product or high moisture content product mainly in the form of

a hydrated coating (Kester and Fennema, 1986). These kinds of coatings are also favored when other barrier properties are researched. Most of these films present interesting oil and gas (oxygen, carbon dioxide) barrier properties at low RH—Relative Humidity—(Albert and Mittal, 2002). Hydrocolloid coatings can also be chemically, enzymatically, and physically treated to improve their moisture resistance (Ou et al., 2005; Tang et al., 2005). Numerous multi-components films based on combination of polysaccharide-protein, polysaccharide-polysaccharide, and/or protein-protein have been developed since the 1990s. Synergetic effects between components, which result from interactions between the macromolecules, such as charge-charge electrostatic linkage, hydrogen bonding, and covalent cross-linking, are researched. The resulting multi-components edible barriers are generally more resistant to water transfer (Gennadios et al., 1993; Parris et al., 1995; Psomiadou et al., 1996). Multi-components films may additionally present improved flexibility (Garcia et al., 2004; Lazaridou and Biliaderis, 2002; Park et al., 2001) and sensorial properties (Longares et al., 2005).

Whatever the type of film-forming material used, plasticizer addition is another method to overcome the problems associated with the use of a single film-forming material, and commonly appears in a moisture barriers formulation. Molecules presenting good moisture barrier aptitudes are usually characterized with low polarity and high linearity. Therefore, they tend to produce films with a high degree of cohesiveness and rigidity (Morillon et al., 2002). Plasticizers, by weakening intermolecular forces between adjacent chains, increase the free volume of the compound and possibility of chain mobility. So doing, plasticizers reduce brittleness, increase flexibility, and elongation at break of edible films. However, they also induce a lowering of the Glass Transition Temperature (Tg) of polymers and enhancement of the diffusion of small molecules, including water, through the barrier film. Plasticizer addition is particularly important when the product is stored at a low RH and/or temperature. Plasticizers used in 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) (Guilbert, 1986).

Composite Films

Pure lipids can be combined with hydrocolloids such as proteins, starches, or celluloses derivatives. 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 resistant matrix of the hydrocolloids. Combination are conducted either 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 DeMulderJohnston, 1997), or by dispersing

solid non-lipid compounds in melted lipids (dispersion technique). Composite films have been extensively reviewed by Wu et al. (2002). The resulting water barrier efficacy of bilayered films is often of the same order of magnitude than that of pure lipid (Debeaufort et al., 2002) and is much higher than that of emulsion-based films or dispersions (Debeaufort et al., 1993; Debeaufort and Voilley, 1995; Martin-Polo et al., 1992; McHugh and Krochta, 1994a; McHugh and Krochta, 1994b).

The addition of non lipid fillers or bulk agents (hydrocolloids, sugar solids) as dispersed components to improve the functional properties of the edible moisture barrier (viscosity, adherence on substrate) is more frequent in commercial and patented coatings/films than in scientific literature. A famous example of solids dispersion is chocolate. Chocolate and derivatives (cocoa-based films) are the most widely used moisture barriers in the confectionery and bakery industries (Morillon et al., 2002; Biquet et al., 1988). The good sensorial properties of chocolate allow the use of thick perceptible coatings that will both resist moisture migration and increase the commercial value of the product. The first comprehensive study on chocolate barrier properties was conducted by Biquet and Labuza (1988). These authors determined the moisture sorption isotherms, effective diffusion coefficient, and water vapor permeability of a dark chocolate film (0.6 to 1.2 mm thick). They reported that a 0.6 mm coating of semisweet dark chocolate used as a barrier coating on a monocomponent system (agar gel) was, in this study, 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 of the chocolate barrier properties were recently proposed (Ghosh, 2003; Ghosh et al., 2004; Ghosh et al., 2002; Ghosh et al., 2005). These authors (Ghosh et al., 2005) investigated the effect of sugars, cocoa powder, emulsifier, and fat type on the moisture resistance (3.5–100% RH, 20°C) of chocolate coatings and underlined the favorable effect of sucrose addition on the barrier moisture resistance. The addition of dispersed saccharides/polysaccharides to enhance the adherence of composite or fat coatings on bakery product was also suggested in various patents (Anonymous, 1979; Haynes et al., 2004; Heuvel et al., 1997; Youcheff et al., 1996).

The addition of various other kinds of inert fillers in fat coating has been similarly suggested in patent literature (Bastiaans and Tap, 2005; Rubenstein and Bank, 1982; Rubenstein and Pelaez, 1986). Inert fillers 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. Generally, addition of fillers in melted fat increases the viscosity of the fat and changes its physical properties in such a way that the water-occluding action is improved. More specifically, the use of an inert filler, such as starch or dextrin, in fat layers improves the coating mechanical property and facilitates its application (application on ice cream cone; Rubenstein and Pelaez, 1986); whereas inorganic fillers, such as silicates, improve the moisture resistance of the barrier. A coating containing inorganic fillers (3–10%) and fat insoluble particles allows for instance, the protection of moisture sensitive food ingredients such as crispy cereals in a chilled but not frozen environment for a prolonged period, i.e. four weeks (Bastiaans and Tap, 2005).

Inorganic Film-Forming Materials

Pure amorphous inorganic compounds-based coatings have been recently presented in the patent literature (Beyer et al., 1996). Used at low thicknesses (0.05 micron or less), such coatings overcome the textural problems associated with the use of organic coatings which have to be applied as a thick layer ($\geq$100 μm for lipid coating) to be effective. Inorganic coatings cover an important range of substances depending on the considered market product regulation. In the United States, for instance, according to Section 21 of the Code of Federal Regulations for edible products (Anonymous, 1977), authorized inorganic compounds gather: silicon dioxide, single silicates, such as sodium, calcium, magnesium, and aluminium silicate, magnesium trisilicate, composite silicates such as sodium-aluminium, potassium-aluminium, and calcium-aluminium silicate, talc, and clay materials such as bentonite, carbon, insoluble carbonates, and phosphates. A favorable effect on breakfast cereals, which become soggy when plunged in milk is an example of application detailed in patent literature: inorganic coating limits cereal hydration and can improve the mineral and nutritional claims. 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 about "edible moisture barrier" deposited over the last twenty-five years (International database, 2006).

ASSESSMENT OF FILM MOISTURE BARRIER PROPERTIES AND ITS CRITICAL POINTS

Modelling Film Moisture Barrier Properties using a Single Permeability Coefficient

Barrier properties of dense, nonporous film and coating materials are generally described through a permeability coefficient assuming that the main physical mechanism of moisture transport is activated diffusion. Considering such mechanism, the permeability of a penetrant through a film depends first on

three factors: i) the nature of the film material, ii) the nature of the penetrant, iii) the interactions between the penetrant and the film. The transport process can be divided into three stages: adsorption of the penetrant on the high concentration side of the film, diffusion of the penetrant through the film under concentration gradient, and desorption of the penetrant on the low concentration side (Rogers et al., 1962).

The Water Vapor Permeability (WVP) of a film is a steady state property which describes the rate of water which passes through the film submitted to a given RH difference. In thin, nonporous, nonswelling, highly hydrophobic film, WVP through a barrier is determined combining Fick's First Law of diffusion (equation 1) and Henry's Law of solubility (equation 2) as expressed in equation 3 (Park, 1995; ASTM, 1980). In this case, WVP is the product of the solubility and the diffusivity coefficients which can be considered as independent from moisture concentration.

$$J = -D \cdot \frac{dC_w}{dx} \tag{1}$$

Where J is the permeate unidirectional flux [g/(m.s)], D the permeate diffusivity corresponding to the rate at which the concentration gradient is dissipated [m^2/s], dC$_w$/dx the local concentration differential.

$$C_w = S \cdot p \tag{2}$$

Where C$_w$ is the concentration of the permeate [mol/m^3], S the solubility coefficient defined as the maximum mass of the migrating molecule that dissolves in a unit volume of the material at equilibrium [mol/(m^3.Pa)], and p the permeate partial pressure in the adjacent air [Pa].

$$WVP = D \cdot S = \frac{J \cdot x}{A \cdot \Delta p \cdot M} \tag{3}$$

Where WVP is the Water Vapor Permeability [mol/(m.s.Pa)], A the surface of barrier [m^2], *M* the water molar weight [g/mol].

As expressed in equation (3) WVP is the result of two parameters: a thermodynamic parameter, whose solubility depends on the compatibility between the penetrant molecule at equilibrium and the material the penetrant is migrating through; a nonthermodynamic kinetic parameter D indicating water mobility in the material and highly influenced by the structural and morphological characteristics of the material.

Modelling Film Moisture Barrier Properties Taking into Account Interactions with Moisture

In all other cases, equation (3) is not verified and WVP is not a sufficient parameter to describe moisture transport through the film. With regard to moisture permeation through hydrophilic, composite, and moderately hydrophobic

films, D and S coefficients vary due to plasticization/swelling consecutive to moisture absorption. As a consequence, in various materials, WVP must be regarded as a function dependent on boundary conditions (McHugh et al., 1993; McHugh and Krochta, 1994c; Morillon et al., 2002). A single value of WVP (often measured with a 0–100% RH difference) can not be considered as an inherent property of the film that ideally reflects its water barrier efficiency for a broad range of testing conditions. On the contrary, WVP is then considered as an inherent property of the couple "penetrant-barrier material" in a given testing configuration (Pasquat, 1986).

Hydrophilic materials such as proteins and polysaccharides present, especially on the high a_w range, much higher moisture sorption isotherms than hydrophobic materials. Water sorption in hydrophilic polymers is usually a nonideal process leading to plasticization and/or clustering phenomena and, as a result, to complex type II or sigmoidal isotherms (Despond et al., 2005). Comparison of a few groups of hydrophilic components based on their moisture sorption has been proposed by some authors. For instance, Buonocore et al.(2005) presented the following classification of hydrophilic components based on increasing moisture sorption isotherm over the full a_w range (25°C): chitosan (MW $\sim$ 310 Da, deacetylation degree >75%) < corn zein (glycerol 20% w/w) < sodium caseinate (glycerol $\sim$40% w/w, cross-linked with transglutaminase) < sodium alginate (cross-linked with CaCl$_2$). It is generally recognized that macromolecules based on hydrophobic monomers present low moisture sorption, i.g. corn zein characterized by high content in nonpolar amino acids, such as leucine, proline, and alanine. However, a general classification of polysaccharides and protein-based films can not be established due to: i) the influence of formulation (degree of polymerization of the macromolecules, presence of lateral groups, addition of plasticizer, addition of non lipid components), ii) the influence of film-forming conditions (pH, thermal treatment, or any cross-linking treatment) and iii) the shift in the relative positions of moisture sorption isotherms over the full range of a_w (Fig. 1).

Fewer classifications of lipids moisture sorption isotherms have been reported (Bourlieu et al., 2006; Callegarin et al., 1997; Higuchi and Aguiar, 1959) which related sorption to the chemical composition of the compounds (presence of polar components, hydrocarbon chain length, number of unsaturations). 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 favor water solubility in the film (McHugh and Krochta, 1994d). This relation is verified since long chain saturated fats, such as alkanes based on aliphatic chains and long chain esters, followed by edible waxes (having again long chain esters as major components), present extremely low moisture sorption isotherms over the full range of a_w.

In hydrophilic, composite, and moderately hydrophobic edible films which present nonlinear water sorption isotherms (Fig. 1) and water-content dependent diffusivities (Fig. 2), WVP values are highly influenced by the RH conditions during testing (location of the RH difference and absolute humidity values; McHugh et al., 1993). Buenocore et al. (2005) recently proposed a model that describes the dependence of WVP to water activity (Equation 4) in hydrophilic film. This model integrated the nonlinear sorption of water of hydrophilic polymer-based film (alginate, casein, chitosan, and zein) and moisture concentration dependence of their effective diffusivity. The model was validated over a 0.3–0.8 a_w range at 20°C. In particular, the moisture sorption isotherms of these polymers were described using the Flory equation and variations of moisture effective diffusivity was considered as an exponential function of the moisture content of the polymer.

$$\text{WVP}_{(aw_1, aw_2)} = \frac{1}{p_0 \cdot (aw_1 - aw_2)} \cdot \int_{C_w(aw_2)}^{C_w(aw_1)} D.dC_w$$

$$= \frac{1}{p_0 \cdot (aw_1 - aw_2)} \cdot \int_{C_w(aw_2)}^{C_w(aw_1)} (D_0 \cdot \exp(\alpha.C_w).dC_w \quad (4)$$
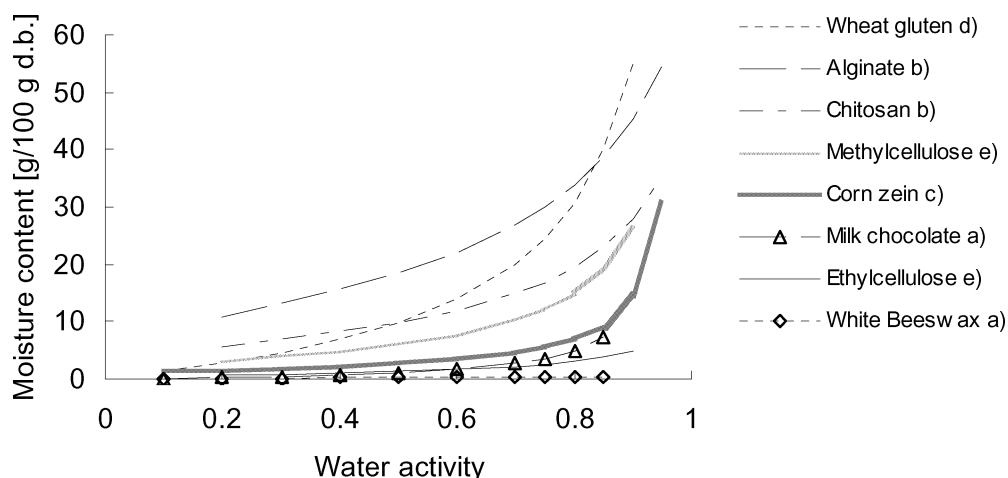

Figure 1 Examples of Guggenheim-Anderson-De-Boer (GAB) fitted moisture sorption isotherms of hydrophilic and hydrophobic barrier films at 20°C reported in literature: a) Bourlieu et al., 2006; b) Despond et al., 2005; c) Lai et Padua, 1998; d) Roy et al., 2000; e)Velazquez et al., 2001.
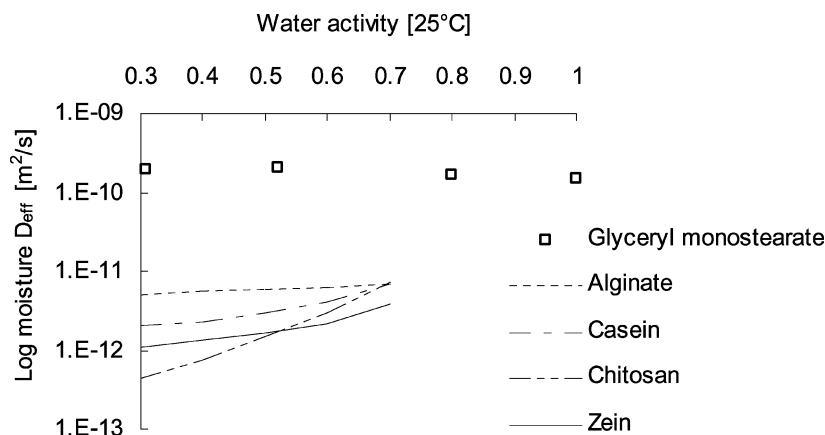
Figure 2 Moisture effective diffusivity (experimental data or model) plotted as a function of water activity (25°C, adapted from a) Buonocore et al., 2005 and b) Higuchi and Aguiar, 1959).

where $WVP_{(aw1,aw2)}$ is the Water Vapor Permeability coefficient for a water activity difference between the upstream and downstream side of the film equal to a_{w1} and a_{w2} respectively, p_0 is water vapor pressure, D is the water diffusion in the polymer at a given moisture content, D_0 is the water diffusion at zero moisture concentration, α is a constant that accounts for the ability of water to plasticize the polymeric matrix, C_w is the polymer moisture content.

For hydrophobic substances, fewer studies have been published. However, since their affinity and interaction with water is limited, their permeability should be less affected by the RH conditions. This has been verified for paraffin wax films (Martin-Polo et al., 1992), and hydrogenated cottonseed oil films (Landmann et al., 1960). Distortions were observed for several other fat materials, including acetyl-stearyl glycerols, milk chocolate, glyceryl monostearate, beeswax, and blends of these last two components (Buonocore et al., 2005; Higuchi and Aguiar, 1959; Landmann et al., 1960). This is attributed to the sorption of water by hydrophilic groups (ester, hydroxyl, carboxyl groups) of the hydrophobic substances, which results in a less dense structure and modifies the film permeability (Morillon et al., 2002). Greener-Donhowe and Fennema (1992) proposed a schematic representation of the water content profile in hydrophobic films containing polar groups submitted either to a 80–100% RH gradient or to a 0–100% RH gradient. For the former gradient the whole film is hydrated and swells whereas for the latter only a limited portion (side exposed to high RH) of the film is modified and explain preserved water barrier properties.

Variation in WVP coefficients have been reported in relation with variations in thicknesses of the barrier film tested. More specifically, hydrophilic films exhibit a positive slope relationship between thickness and WVP. This relationship has even been reported to be exponential for some materials (McHugh et al., 1993).

If several explanations have been provided for such influence between WVP and thicknesses, some focusing on structural aspects: i) the barrier film thickness can influence the barrier film structure and its homogeneity; other focussing on limit layer

impact: ii) air gap between the solution and films lead to equilibrium moisture relationships at film/air interface differing from test cup solution equilibrium conditions, increase in thickness lowers the effect of such limit layers; generally admitted explanations are related to nonlinear moisture sorption in the barrier film: iii) increased thickness lead to a higher quantity of hydrophilic component which may interact with water molecules causing swelling and apparent thickness effect (Mac Hugh et al., 1993).

Yoshida et al. (2005) explained the thickness effect in whey protein films by the increased moisture sorption of thicker films. These authors quantified the moisture absorbed by films of increasing thicknesses (289 μm, 369 μm, and 448 μm) during a diffusion process (0–75% RH, 25°C). A model considering the water absorbed by the film during the diffusion process as linearly proportional to the added concentration of moisture in the film was validated. The model described the diffusion-absorption phenomenon using equation (5) derived from Fick's Second Law:

$$\frac{\partial C_w'}{\partial t} = D_{eff} \cdot \frac{\partial^2 C_w'}{\partial x^2} - \lambda C_w' \tag{5}$$

where, $C_w(x, t)$ is the local moisture content of the film, C_{w0} the initial moisture content, $C_w'(x, t)$ the local added moisture concentration defined equal to $C_w(x, t) - C_{w0}$, D_{eff} the moisture effective diffusivity in the film and λ a constant parameter.

Considering a steady state regime in the whey film and specific boundary conditions, an effective diffusivity of 2.25×10^{-13} m$^2 \cdot$s^{-1} which was independent of film thickness was determined.

In composite and hydrophobic barriers, the relationship between thickness and WVP is not that clear. Martin-Polo et al. (1992) reported a decrease in the permeability of cellophane films coated with paraffin wax or oil when its thickness was increased from 30 to 60 μm which then remained almost constant with increasing thickness up to 120 μm. The same decreasing trends were observed by Debeaufort et al. (2000b) for

triglyceride layers and for paraffin-based films. In chocolate, Biquet and Labuza (1988) observed a decrease in dark chocolate films WVP when its thickness was increased from 600 to 900 μm and an increase in WVP from 900 to 1200 μm. Similar observations were reported on cocoa butter and on acyl stearyl glycerol (Landmann et al., 1960; Lovegren and Feuge, 1954). These observations seem to confirm that below a critical thickness WVP increases due to the presence of defects and less favorable structure in thin barrier films. Above this threshold, which depends on the film composition and mode of application, similar homogeneity can be expected and anomalous behavior can only be explained by increased nonlinear phenomena (swelling and sorption) due to the increased amount of hydrophilic groups that may interact with water. In a more recent study (Guillard et al., 2004a), the resistance to moisture transfer in situ (film put at the interface of a sponge cake/agar gel system) of an acetylated monoglyceride film remained constant when its thickness was increased from 200 to 1500 μm. However, the film efficiency was estimating this time using a Fickian model considering nonlinear sorption of water in the barrier film and constant moisture D_{eff}. This hypothesis is in agreement with Yoshida's results (2005), in moderately hydrophilic films presenting similar integrity (which can be reasonably assumed above a threshold of 200 μm), when taking into account the nonlinear sorption of water by the barrier, the moisture D_{eff} can be considered as almost constant.

Variations of thickness during moisture transport due to swelling, are especially important for hydrophilic compounds. Roca et al. (2007) analyzed moisture sorption in hydrophobic (acetylated monoglyceride), hydrophilic (wheat gluten), and solid dispersion (dark chocolate) barrier matrixes using a Fickian model. These authors compared moisture D_{eff} values determined in the material using either a numerical solution, taking into account deformation of the material consecutive to sorption, or an analytical solution. Using a numerical solution, a simplified deformation mechanism was assumed: the deformation of the barrier was unidirectional, instantaneous, and equal to the variation of volume occupied by the liquid phase. The effect of deformation hypothesis on the D_{eff} value identified was negligible in the lipid matrix, but had a strong impact on the D_{eff} for the hydrophilic barrier and solid dispersion: D_{eff} were higher when calculated using the model with deformation assumption, respectively increasing from 0.9×10^{-11} to 1.4×10^{-11} m^2/s and from 0.9×10^{-12} to 1.3×10^{-12} m^2/s. These differences were explained by the fact that the analytical solution to Fick's second law, assuming no swelling of the solid matrix, underestimates the thickness of the product when water activity increases. More recently, Magnetic Resonance Imaging (MRI) studies of moisture sorption through thermoplastic starch shed light on the mechanism of swelling of such material (Russo et al., 2006). The MRI technique was advantageously used to monitor microscopic changes in the cross section of the polymer without any physical slicing of this latter. The solvent front was directly visualized. This front is the boundary that separates swollen from unpenetrated material throughout

the cross-section of the polymer. The diffusion coefficient was directly calculated from the concentration profile obtained by MRI images using an unidirectional Fickian model applied to the rectangular sample of polymer. The model considered an exponential dependence of the D_{eff} on the moisture concentration in the film (equation 6):

$$D_{eff} = D_0 \cdot e^{A(C_w/C_{w0})} \tag{6}$$

where C_w is the moisture concentration at a point, C_{w0} is the concentration at the surface, D_0 and A are constants.

The swelling of the polymer, defined as the increase in the sample thickness relative to the sample initial thickness, was accurately fitted using the following equation:

$$S = S_{max}(1 - e^{-kt}) \tag{7}$$

where S is the swelling at time t, S_{max} is the maximum swelling as time approaches ∞, and k is the rate of swelling. The swelling phenomenon was integrated in the diffusion rate and informative on the glassy core change of state.

Testing Procedures to Determine Water Vapor Permeability, Moisture Sorption and Diffusivity in Edible Films – Classifications Based on these Properties

WVP measurements are easy to conduct using simple gravimetric methods of measurement. These methods consist of monitoring mass change versus time of a permeation cell hermetically sealed with the barrier film. The permeation cell contains a desiccant or saturated solution and is stored in a desiccator in which a given RH is imposed. Standard procedures are detailed in the American ASTM E96-80 (1980). Reliable methodologies are extremely important in that permeability values are commonly used in product shelf-life predictions, as well as in tailoring film permeability for specific food applications. Therefore, several researchers focused their efforts on measuring WVP through film materials (Table 3). Comprehensive tables of WVP values have been recently proposed by Morillon et al. (2002) and Wu et al. (2002). Table 3 adapted from Saravacos and Maroulis (2001) summarizes the range of moisture WVP values encountered in food coating in comparison with polymeric packaging at 20°C.

To determine more precisely the characteristics of moisture transfer within the film, solubility, and diffusivity should be determined. For solubility, sorption, and desorption isotherms measurements are conducted. Common methods are based on the similar principles than for WVP gravimetric measurements: maintaining a controlled RH atmosphere around the product and measuring its gain or loss of mass with time (Bell and Labuza, 2000). However, these measurements are often time consuming especially when static methods, e.g. the saturated salt solutions method, are used since they require long equilibrium

Table 3 Comparison of moisture WVP (20°C) ranges for edible coatings in comparison with most commonly used synthetic packaging films (Adapted from Saravacos and Maroulis, 2001)

Film or coating	WVP [10^{-11}g.(m.s.Pa)$^{-1}$]	RH difference [%]	Thickness [mm]	Temperature [°C]	Reference
Synthetic films					
Aluminium	0.0005	0–98	(−)	38	(Myers et al., 1961)
HPDE	0.002	0–100	0.019	27.6	(Shellhammer and Krochta, 1997a)
LPDE	0.014		0.010	27.6	
PP	0.010		0.025	25	
PVC	0.041		0.012	27.6	
Lipid films	0.03–1.0	0–100		20	
Waxes					
Candelilla wax	0.014	0–100	0.14	24.9	(Shellhammer and Krochta, 1997a)
Paraffin	0.023		0.66	25	(Lovegren and Feuge, 1954)
Beeswax	0.103		0.14	25.9	(Shellhammer and Krochta, 1997a)
Carnauba wax	0.114		0.130	27.5	
Fatty acids					
Capric acid	0.38	12–56			(Koelsch and Labuza, 1992)
Palmitic acid	0.65				
Stearic acid	0.22				
Triglycerides and derivatives					
Tripalmitin	0.225	0–100	0.130	27.5	(Shellhammer and Krochta, 1997a)
Triolein	12.100	22.84		25	(Quezada Gallo, 1999)
Anhydrous milkfat	1.028	0–100	0.130	24.9	(Shellhammer and Krochta, 1997)
Hydrogenated peanut oil	3.863		3.39	25	(Lovegren and Feuge, 1954)
Glyceryl monostearate	0.77		1.026	24.3	(Higuchi and Aguiar, 1959)
Acetomonopalmitine	11.35		0.200	20	(Bourlieu et al., 2006)
Tempered cocoa butter	26.8–61.2		1.59–2.92	26.7	(Landmann et al., 1960)
Milk chocolate	88.99		0.68	20	(Bourlieu et al., 2006)
Protein films	1.0–100.0	0–100		20	
Wheat Gluten	12.97	0–100	0.053	20	(Guillard et al., 2003)
Soya	281.18	50–66	0.072	25	(Rhim et al., 2002)
Corn zein	11.6	0–85	0.12–0.33	21	(Park and Chinnan, 1995)
Polysaccharide films	1.0–10.0	0–100		20	
Cellulose derivatives	9.2–11.0	0–85	0.04–0.07	21	(Park and Chinnan, 1995)
Starch	25–78	11–100	0.005–0180	30	(Bertuzzi et al., 2007)

time (Table 4). Commercially available dynamic microbalances allow using thinner samples and reduction of time of equilibration. The advantages and drawbacks of various other methods for sorption measurements using volumetric, optical, pressure radiotracer have been described by other investigators (Felder and Huvard, 1980) and are beyond the scope of this review.

With regard to the diffusion coefficient D, that represents the kinetic parameter of moisture transfer, no direct measurement can be performed. Diffusivity must be identified from moisture transfer kinetics through the film in permeation or sorption configuration using variable experimental sets-up (Boudhrioua et al., 2003; Doulia et al., 2000; Zogzas et al., 1994). Moisture Diffusivity determination requires the establishment of hypothesis on the main physical mechanism of transport, influence of boundary conditions on diffusivity, development of mathematical models, and use of optimization algorithms. Most of the analyses of mass transfer through edible coatings rely on the theory of diffusion in solids as outlined in the texts by Crank (1975) and Geankopolis (1983). Crank presented a number of analytical solutions to Fick's Second Law applied to the element of variable geometry (infinite slab, cylinder, and sphere with radial diffusion) with specific initial and boundaries conditions, considering in the simpler models a diffusivity coefficient

which was constant and valid on all the integration domain, or on the contrary, variable diffusivity coefficients. As Fickian models are not strictly representative of the various prevailing mechanisms of water transport in food products, the identified diffusion coefficient is considered as an apparent or effective diffusivity (D_{eff}).

The simplest models of determination, considering D_{eff} constant over the range of a_w studied, were first applied to edible films by Higuchi and Aguiar (1959). These authors determined moisture D_{eff} in various cellulose derivatives and lipid films using permeation kinetics. The films were supposed to be infinite slabs with uniform initial moisture concentration submitted to two different constant surface concentrations and through which moisture transfer has reached a steady-state. An analytical solution of Fick's Second Law proposed by Crank, known as the Time-Lag method, was used to calculate the moisture D_{eff} in the barriers. Although a convenient and relatively simple means of evaluating the kinetic parameter of transfer in barrier films, the Time-Lag method has some major drawbacks which limits its accuracy: dependency of D_{eff} on moisture concentration not considered in the model, measurements in transient state instead of permanent state inducing underestimation of the D_{eff} value, erroneous assumption on concentration of

Table 4 Examples of Guggenheim-Anderson-De-Boer (GAB) fitted moisture sorption isotherms of hydrophilic and hydrophobic barrier films reported in literature

Barrier film	Xo [g/g d.b.]	Cg	K	Method of isotherm determination	a_w range	T [°C]	Evaluation of fitting	Method of determination of dry matter	Reference
Wheat gluten	0.0933	1.3733	0.9442	Static SS[#] method	0.11–0.84	25	G = 7.24[§]	Dessiccation over anhydrous $CaSO_4$	(Roy et al., 2000)
Alginate*	0.1160	17.6800	0.832	Setaram B92 microbalance[‡]	0.21–0.97	20	RSS = 0.64[§§]	Desorption under vacuum (2×10^{-6} mBar)	(Despond et al., 2005)
Chitosan**	0.0590	18.2300	0.879				RSS = 4.05×10^{-4}		
Methylcellulose	0.0352	11.0973	0.9642	Static SS Microclime method	0.22–0.90	20	$R^2 = 0.9957$[¶]	Oven dessiccation 10 hours 105°C	(Velazquez et al., 2001)
Ethylcellulose	0.0091	4.4003	0.9109				$R^2 = 0.9811$		
White chocolate	0.0090	2.7925	1.08	SS and DVS[‡‡] methods	0.11–0.75	20	RMSE = 2.89×10^{-2}[¶¶]	Dessiccation over P_2O_5	(Bourlieu et al., 2006)
Dark chocolate	0.0064	3.5336	1.0489				3.88E-02		
Milk chocolate	0.0097	1.0967	1.0363				4.07E-02		
Monoacetopalmitin	0.0796	0.1868	0.5191				1.30E-03		
Wax/ACETEM	0.0085	1.2351	0.7893				4.11E-02		
Beeswax	0.0100	0.9949	0.3821				3.98E-02		
Barrier fat	0.0005	27.4149	0.9389				7.00E-04		

*Mannuronic/Guluronic residue ratio: 0.8; **Acetylation Degree : 0.8; [#]SS: equilibrium over Saturated Salt solutions; [‡] Setaram B92 dynamic microbalane submitting sample at given temperature and increasing partial pressure of water by means of an evaporator; [‡‡] DVS: Dynamic Vapor sorption balance submitting sample at given temperature and increasing RH levels; [§]$G = \frac{100}{n} \cdot \sum \frac{|Xe - Xp|}{Xe}$; [§§]$RSS = \sum (Xe - Xp)^2$; [¶]$R^2$ = linear correlation coefficient; [¶¶]$RMSE = \sqrt{\frac{(Xp - Xe)^2}{(N - p)}}$ where Xe, Xp, N, and p are respectively, the experimental and predicted moisture content [g/100 g d.b.], the number of experimental moisture content measurements and the number of estimated model parameters.

moisture in the permeation cell (Ghosh, 2003; Rumsey and Krochta, 1994). Some even simpler models based on the "permeability/diffusivity/solubility" relation of equation (3) and also considering the moisture D_{eff} constant over the range of water activity investigated, were applied by various authors (Table 5). Such models allowed deducing the average effective moisture diffusivity in a barrier material in which the moisture sorption was already known. Such simplification implied a linear moisture sorption isotherm and constant D_{eff} over the a_w difference, which were abusive assumptions especially for hydrophilic barriers.

The most recent studies used an algorithm that considered moisture D_{eff} constant only on a limited portion of the integration range and thus gave access to curves of variation of moisture D_{eff} on a given water activity range.

All the D_{eff} values reported in literature for edible coatings are summarized in Table 5. This table points out the variability in D_{eff} determination methods, both in collection and analysis of data. Influence of treatment of data on the D_{eff} values is well illustrated on dark chocolate for which different D_{eff} values are identified depending on the hypothesis considered to describe the transfer. More generally, D_{eff} values reported in edible films vary from high values (10^{-10} m^2/s) to extremely low values similar to those reported in inorganic polymers (PET fibers = 0.1×10^{-12} m^2/s, Gouanvé et al., 2007; HPDE = 0.5×10^{-12} m^2/s at 20°C, Saravacos and Maroulis, 2001).

As it has been outlined in the previous section, for a majority of edible film which can not be considered as purely hydrophobic, WVP values are only estimated parameters which reflect barrier film efficiency in a given testing conditions and have to be considered with precaution. Systematic measurements of the moisture sorption and D_{eff} in barrier films should be conducted as frequently as possible and effort of standardization of methods of measurement should be undertaken to build a useful database.

In addition to the influence of chemical composition and condition of testing (thickness of the barrier, range of the RH and RH difference value), physical state, structure, and temperature influence moisture sorption, effective diffusivity, and the resultant moisture barrier properties of edible films. A study of the influence of these factors on the barrier properties of lipid-based films have been proposed by Shellhammer et al. (1997a) and Morillon et al. (2002). The formal, mechanistic, or empirical models reported in literature to describe influences of these factors on moisture transport through barrier materials are reviewed below.

Relationship between Film Moisture Barrier Properties and its Structure

In an as large an extent as chemical composition, physical state, and structural characteristics of the barrier material highly influence its performance. Physical state and structure are themselves conditioned by composition, conditions of testing (RH, temperature, pressure), and also by the barrier preparation technique.

Factors which affect the "tightness" of the molecular structure of the film material network, i.e. mainly its free volume, cohesive energy density, and crystallinity, significantly influence moisture diffusivity, moisture sorption, and thus the permeability of the barrier. This influence is easy to understand considering the diffusion process "as a series of activated jumps from a vaguely defined cavity to another" as it has been described by Rogers (1985). Qualitatively, the diffusion rate increases with the increase of the number or the size of cavities caused for instance by the presence of substances such as plasticizers. On the other hand, structural entities such as crosslinks or degree of crystallinity decrease the size or number of cavities and thereby the diffusion rate (Chao and Rizvi, 1988). Cussler (1984) integrated the influence of pores of the moisture effective diffusivity of a material consisting otherwise of an impermeable solid using equation (8):

$$D_{eff} = D \cdot \frac{\varepsilon}{\tau} \tag{8}$$

where D is the moisture Diffusion coefficient within the pores of the material, ε the void fraction or porosity of the solid and τ the tortuosity of the pores. The range of values for τ varies from 3 to 10 in highly heterogeneous materials. Tortuosity is mainly considered as an empirical factor of correction affecting D_{eff} for which various geometric definitions have been given in literature (Gekas, 1992).

The degree of crystallinity of a material (or solid fat content for lipids) is an important parameter which influences its moisture barrier properties. It is generally assumed that crystalline materials are totally impermeable to small molecules and thus, to water. Indeed, a crystalline state is characterized by an extremely low moisture sorption (limited to the surface of the crystals) and extremely low D_{eff} due to fixed and ordered configuration of the molecules. Hydrophobic crystals are totally insoluble in water whereas hydrophilic crystals are characterized by a type III moisture sorption isotherm (Bell et al., 2000) presenting a sharp increase in sorption subsequent to crystal dissolution. Most of the barrier materials are only partially crystalline. Models of transfer thus considered that moisture transport takes place mainly through the noncrystalline fraction of the material: i.e. in the amorphous fraction for polymers and in the liquid fraction for lipids. In addition to the degree of crystallinity of the material, the size and spatial distribution of crystals on one hand and intercrystalline packing arrangement on the other hand have major consequences on the barrier properties of the material (Martini et al., 2006). Various mechanistic models have been proposed to describe moisture transport through a partially crystalline matrix. The simplest models considered moisture transfer through the crystalline fraction slow enough to be neglected and expressed WVP through a semi-crystalline

Table 5 Values of moisture effective diffusivities in edible coatings reported in literature and their method of determination

Edible coating composition	Method	Moiture D_{eff} values [$\times 10^{-12}$ m^2/s]	References
Ethylcellulose (DS[#]: 2.5 and 1.7)	Average value estimated from permability and solubility data according to P = DxS;	19.5, 4.9	(Beck et al.,1996)
Ethylcellulose (DS: 1.7 + diethyl tartaric acid)		8.4	
Zein (+ diethyl tartaric acid)		0.8	
Wheat gluten (Vital wheat gluten/glycerol, 2.5 :1)	Average value estimated from permability and solubility data according to P = DxS; adsorption; RH difference: 0–75%	116 $\times 10^{-12}$ g/s	(Roy et al., 2000)
Whey protein (whey protein 55.18, glycerol 17.06%, moisture 17.76%); 297 μm thick	Numerical solution (Fourrier series) of equation of diffusion with gravitation drift in a permeable slab. Adsorption RH difference 50–75%, 25°C	0.51	(Yoshida et al., 2003)
Hydrophylic polymers (alginate, casein, zein, chitosan)	Combination of Flory equation and equation X; Adorption RH difference 0–70%; 0.05% steps; 25°C	0.43 to 7.20	(Buonocore et al., 2005)
Lipid edible barriers:	Time lag method coating considered ∼ infinite slab in permeation; Adsorption; 24.5 °C	Respectively 194; 206; 165; 145	(Higuchi and Aguiar, 1959)
Glyceryl monostearate (GM) - 1.0 mm	RH difference 0–100%; 0–80%; 0–52%; 0–31%		
GM - beeswax (70/30)- 2.2 mm	RH difference 0–100%	86.4	
Glyceryl di-stearate- beeswax (70/30)- 2.1 mm		0.97	
Glyceryl tristearate- beeswax (70/30)- 1.1 mm		0.78	
Glyceryl tristearate- beeswax (50/50)- 1.0 mm		53.6	
Cellulose triacetate- 1.52 mm		0.21 to 0.12	
Dark chocolate (29.6% cocoa butter, 51.4% sucrose, 18.5% cocoa solids, 0.4% moisture); ∼600 μm thick	Time lag method, coating considered ∼infinite slab in permeation; Adsorption; RH difference 0–75%; 0–65%; 20°C	Respectively 0.11 and 0.08	(Biquet and Labuza, 1988)
	Analytical solution of equation of diffusion with gravitation drift in a permeable slab. Adsorption RH difference 0–75%; 20°C	0.26	(Antunes and de Avellar, 2003)
Coconut oil-based coatings	Time lag method coating considered ∼ infinite slab in permeation; Adsorption RH difference 0–75%; 18.5°C		(Ghosh, 2003)
coconut oil - 2.00		39.6	
coconut oil/ lecithin – 1.86		34.1	
coconut oil/30% sugar – 1.93		19.0	
coconut oil/40% sugar – 1.83		15.4	
coconut oil/30% sugar/0.5% lecithin - 2.04		5.80	
coconut oil/40% sugar/0.5% lecithin - 1.97		4.27	
coconut oil/2.5% cocoa powder – 0.81		11.4	
coconut oil/20% cocoa powder – 0.74		11.9	
coconut oil/30% cocoa powder – 0.87		12.6	
coconut oil/40% cocoa powder – 0.90		5.72	
coconut oil/20% cocoa powder/ 0.5% lecithin - 0.86		16.2	
coconut oil/30% cocoa powder/ 0.5% lecithin – 0.87		15.6	
coconut oil/40% cocoa powder/ 0.5% lecithin – 0.90		1.16	
Acetylated monoglycerides (acetylation degree varying from 30 to 70%, chain length C14 to C20)	Analytical solution of Fick's second law, coating considered ∼ infinite slab; adsorption in unsteady state; 12 steps for a global RH difference 0–100%; 20°C	17.3 to 28.0	(Guillard et al., 2003)
Acetylated monoglycerides	Numerical solution of Fick's 2nd law, coating considered ∼ infinite slab; adsorption in unsteady state;deformation and external resistance hypothesis; RH difference 0–100%; 20°C	9.3	(Roca et al., 2007)
Dark chocolate		98	
Wheat gluten		1.9	

[#] DS: Degree of Substitution

polymer as equal to:

$$WVP_p = \frac{x_a \cdot S_a \cdot D_a}{h \cdot b} \qquad (9)$$

where x_a, S_a and D_a are the respective fraction, solubility and diffusivity of the amorphous phase; h is a geometric factor connected with the length and cross-section of the diffusion trace; and b is the mobility of chain segment associated with the crystalline linkage (Kumins, 1965).

An analogy between small solutes transport and electrical conductivity allowed the application of Maxwell equation to describe moisture diffusivity (D_{ss}) in a dilute heterogeneous matrix at steady-state (Falla et al., 1996; Maxwell, 1881):

$$\frac{D_{ss}}{D_0} = \frac{\frac{2}{D_s} + \frac{1}{D_0} - 2\phi \cdot \left(\frac{1}{D_s} - \frac{1}{D_0}\right)}{\frac{2}{D_s} + \frac{1}{D_0} + \phi \cdot \left(\frac{1}{D_s} - \frac{1}{D_0}\right)} \qquad (10)$$

where D_0 is the diffusion coefficient through the continuous media, D_s is the diffusion coefficient through the spheres, and Φ is the volume fraction of the sphere in the composite material. The assumption in this derivation is that the content of sphere is low enough to ensure that no direct contact exists between neighbouring spheres. Maxwell equation was initially established to predict electrical conductivity of a system of low conducting sphere in a high conducting matrix.

If the particles do not take part in the diffusion process, which can be assumed for crystalline particles, i.e. $D_s \to 0$, equation 10 becomes:

$$\frac{D_{ss}}{D_0} = \frac{2(1 - \phi)}{2 + \phi} \qquad (11)$$

Equation 11 was validated on solid dispersions (chocolate flavored coating) including a variable amount of crystalline sucrose (Ghosh, 2003).

Equation 10 can also be used to predict the moisture transport through heterogeneous media including spheres in which moisture diffusion is extremely rapid compared to the continuous media, in this case, $D_s \to \infty$:

$$\frac{D_{ss}}{D_0} = \frac{1 + 2_\phi}{1 - \phi} \qquad (12)$$

In a purely amorphous matrix such as polymers, the matrix physical state influences both water diffusion rate and the polymer relaxation rate leading to variable diffusion mechanisms (Masaro and Zhu, 1999). The initial part of sorption of water per unit area of polymer at time t (M_t) compared the sorption at equilibrium at a given RH (M_∞) can be fitted to an empirical equation :

$$\frac{M_t}{M_\infty} = kt^n \qquad (13)$$

where k is a constant and n a parameter related to the diffusion mechanism, the value of which lies between 0.5 and 1.

The value of the n parameter indicates the type of diffusion mechanism: three different cases have been reported. For the first one, corresponding to Fickian transport, the polymer is in a rubbery state, the polymers chains have a high mobility that allows an easy penetration of moisture. Therefore, the rate of diffusion is much lower than the rate of relaxation, and n is equal to 0.5. Fickian diffusion can be observed in plasticized polymer systems and was for instance reported in chitosan films (Despond et al., 2005). Non-Fickian diffusion processes are mainly observed in glassy polymers, i.e. when the temperature of the study is below the Tg and the polymer chains are not sufficiently mobile to permit immediate penetration of the solvent in the polymer core. Two kinds of non-Fickian diffusion mechanisms are defined: a first mechanism for which n is equal to 1 and in which diffusion is very fast compared to the rate of relaxation (case II diffusion); a second mechanism, in which the moisture diffusion and the polymer relaxation rate are almost of the same order of magnitude, called anomalous diffusion with n values lying between 0.5 and 1.

The preparation technique of the barrier film is another parameter that may influence the barrier material physical state, its structure, and is likely to have effects on its barrier properties. Several authors studied the influence of the preparation technique on the performance of multi-component edible films including lipids (Debeaufort et al., 1993; Donhowe and Fennema, 1992; Gontard et al., 1994; Greener Donhowe, 1992; Greener and Fennema, 1989a; Greener and Fennema, 1989b; Kester and Fennema, 1989a; Kester and Fennema, 1989b). One of the earlier studies was conducted by Fox (1958) who studied the Water Vapor Transmission Rate of cellophane covered with paraffin waxes. These authors reported an important effect of the cooling rate on the crystalline structure of the wax: shock cooling the wax in cold water ($\sim 2°C$) gave rise to small unoriented wax crystals, which presented numerous small fissures or microscopic defects. Most of the other works specially focused on the comparison of efficacy between emulsified films and bilayered structures (Kamper and Fennema, 1985; Martin-Polo et al., 1992). These works pointed out the superior water barrier efficacy of bilayered films compared to emulsion-based films (Debeaufort et al., 1993). This result is again in agreement with an electrical analogy: the resistance to moisture transfer of the lipid-coated film is the sum of the resistances of the individual layers whereas the global resistance R_e of an emulsion-based barrier (corresponding to electrical resistance assembled in parallel) can be obtained according to equation (14):

$$\frac{1}{R_e} = \frac{1}{R_C} + \frac{1}{R_d} \qquad (14)$$

where R_c and R_d are respectively the moisture transfer resistance of the continuous phase and dispersed phase (Debeaufort, 1993). Depending on the volume fraction of each phase and on their

geometry, equations derived from Maxwell theories such as (10) can also be applied.

More recently Bravin et al. (2004; 2006) investigated the influence of spraying on the WVP (RH difference 22–65%, 22–85%) and structure of emulsified films composed of corn starch, methyl cellulose, and soya oil. The coating obtained by spraying presented a WVP value not significantly different from the self-supported film obtained by casting over a glass plate (6.48 vs 6.80×10^{-12} mol.(m.Pa.s)$^{-1}$). Coatings sprayed at higher pressure (3.5 bar) presented higher WVP. This could be explained by a higher mechanical stress which induced irreversible structural change of the polymeric-lipid dispersion. Fewer authors focused on the effect of the preparation technique on the efficiency of pure lipid films. Guillard et al. (2004a) compared the efficacy of self-supported and formed-in-place (by spraying or by brushing on the surface of a sponge cake) coatings of acetomonopalmitin to reduce moisture transfer in composite system (0.99 a_w agar gel/0.84 a_w sponge cake). For formed-in-place coatings, a significant decrease in the efficiency of film compared to a self-supported structure was reported. The moisture D_{eff} value in the formed in place coating was 24 times higher than in the self-supported film. This important difference underlines the difficulty of forming a good barrier film on irregular food surfaces.

The cooling rate applied during fat coating preparation is another factor which affect the lipid-based barrier structure and more specifically crystal habit (polymorphism of the solid state, crystallites size and shape, spatial distribution of the network mass). However, it has received little attention except for chocolate and cocoa butter in which it was demonstrated that a proper tempering gives rise to a denser, less porous structure with a lower WVP, than when the fat is badly tempered (Loisel et al., 1997). Martini et al. (2006) also studied the effect of processing conditions on the structure, the physicochemical characteristics, and WVP of four low melting point fat samples: partially Hydrogenated Palm Kernel Oil (HPKO) blended with canola oil, partially HPKO blended with canola oil plus an emulsifier, distilled monoglycerides, and a commercial fat (Benefat). The processing conditions studied consisted of three cooling rates (50°C/mn, 30°C/mn, 10°C/mn) without shearing the fat materials and the intermediate cooling rate combined with shearing. Processing conditions only affected the microstructure of the fats containing HPKO but not of the two others. Processing conditions did not significantly affect the WVP of the fat samples. However, crystals domain size (influenced by crystallization conditions for some of the fats) and SFC were pointed out as important factors controlling water vapor migration. These authors proposed a mechanistic model (Equation 15) to relate WVP of a fat material to its structural characteristic:

$$\frac{WVP}{WVP_{max}} = e^{-\alpha(\varepsilon/d)\phi} \qquad (15)$$

where WVP is the Water Vapor Permeability of the fat material [mol/(m.s.Pa)], WVP_{max} the Water Vapor Permeability of the oil

in the absence of solids for $\Phi = 0$ [mol/(m.s.Pa)], Φ the volume fraction of solid (or SFC [%]), the ratio of the crystal domain size ξ [Å] to the lamellar spacing d [Å], α a parameter related to the tortuosity of the diffusional path through the crystal network. ξ is calculated from the full width half maximum of the different X-ray reflections in q space.

Mechanistic models are typically used to provide methods for determining how transport is affected by the film structure and composition and by physico-chemical interactions between the penetrant and the film. When adequately tested and verified, they provide reliable prediction of the permeation behavior (Chao and Rizvi, 1988). This mechanistic model was tested here only on four fats presenting similar melting point and for a given WVP configuration (5°C, 95–33% RH difference). Further validation of the mechanistic model would have been interesting (other fats, at higher temperature corresponding to another SFC in the barrier material). The model hypotheses are thus only valid over a narrow range of conditions.

Influence of Temperature on Film Moisture Barrier Properties

Increasing temperature increases molecular mobility and diffusivity. Hence, it induces accelerated movement of water through barrier matrixes. As long as the coating structure is not modified, the dependence of diffusion, sorption, and permeability coefficients on temperature can be expressed by Arrhenius Law (Equations 16 to 18; Rogers, 1985):

$$P = P_o \exp\left(-\frac{E_{a,p}}{RT}\right) \qquad (16)$$

$$D = D^* \exp\left(-\frac{E_{a,D}}{RT}\right) \qquad (17)$$

$$S = S_o \exp(-\Delta H_s / RT) \qquad (18)$$

Where $E_{a,p}$ and $E_{a,D}$ are the Activation Energy for the permeation and diffusion process (kJ/mol), ΔH_s is the heat of sorption (kJ/mol), R the gas perfect constant (8.314 J/mol/K), T, temperature (K) and D^*, P_o, S_o the pre-exponential factors for the three processes.

If both moisture diffusion coefficient and solubility are constant over the range of water activity investigated (equation 3 verified), the energy of activation of permeability can thus be obtained from the relation:

$$E_{a,p} = E_{a,D} + \Delta H_s \qquad (19)$$

The favorable interaction between moisture and polar polymers generally results in a negative ΔH_s (exothermic adsorption) and thus, in a decreasing equilibrium water sorption with temperature. However, the inverse phenomenon has been

Table 6 Energy of activation of WVP ($E_{a,p}$) of various moisture barriers reported in literature (Adapted from (Debeaufort et al., 2002)

Film composition	Range of temperature [°C]	$rmEa, p$[kJ.mol^{-1}]	References
Tristearin	25–40	−24.6	(Fennema and Kester, 1991)
Stearic acid	25–40	−23.4	
Hexatriacontane	25–40	−23.8	
Gluten+glycerol	5–35	−15.0	(Gennadios et al., 1994)
Soy protein + glycerol	5–35	−16.5	
Triolein	25–45	−21.7	(Quezada Gallo, 1999)
Paraffin wax + glycerol monostearate	25–45	−22.0	
Candelilla wax	25–40	17.0	(Greener Donhowe and Fennema, 1993)
Carnauba wax	25–40	21.0	
Beeswax	25–40	29.0	
Hydrogenated palm oil + glycerol monostearate	25–40	50.2	(Quezada Gallo, 1999)
Methylcellulose + polyethylene glycol 400	25–40	46	(Debeaufort et al., 1993)
Acetylated monoglyceride	5–35	43.7	(Guillard et al., 2004b)

observed in high fat content products as for example in oleic and peanut oil (Loncin et al., 1968) and in acetylated mono and diglycerides (Guillard et al., 2003). Conversely, water vapor diffusion is always a thermally-activated process with positive $E_{a,D}$. With regard to WVP, the resulting $E_{a,P}$ can be negative or positive both for hydrophilic or hydrophobic barrier films as reported in Table 6. $E_{a,P}$ depends on the predominant mechanism involved in moisture transport through the film and resultant between ΔH_s and $E_{a,D}$.

As it has been described in a previous section, a large range of WVP values for a similar barrier have been reported in the literature by different authors. Some of the discrepancies between WVP values obtained for a similar barrier material by different authors and can be explained by differences in the experimental set up of measurements. Standard procedures for WVP measurements should lead to normalized methods. However, the procedures were often adapted by authors to test the barriers in conditions closer to their target applications. These adaptations resulted in a higher variability of the systems reported in the literature which present variable cell sizes, barrier thicknesses, or surface of permeation and are not necessarily ventilated. This last point can give rise to problems of limit layers influencing the permeability results for hydrophilic compounds (Bourlieu et al., 2006). These problems of air gaps can be corrected a posteriori following the procedure proposed by Mac Hugh et al. (1993). The direction of the water flow (from the inside of the permeation cup toward the outside or the contrary) may also influence the WVP values as it was reported for chocolate (Biquet and Labuza, 1988). This anomaly was explained and modelled by Antunes and De Avellar (2003) using a theoretical model combining Fickian diffusion with an additional contribution of gravitational drift. This model fitted accurately the data obtained by Biquet et Labuza (1988). Such contribution is highly dependent on the barrier film structure and was not observed on moisture sorption kinetics for a more homogeneous barrier matrix of whey protein (Yoshida et al., 2002).

The influences of the testing factors on the WVP, D_{eff} and moisture sorption values underline the limit of using these parameters on their own to predict barrier film behavior for a specific application. Several formal and mechanistic models have

been reported which describe the influence of some of the testing factor on the moisture transport through the barrier. However, these models are generally only valid for a narrow range of testing conditions and do not integrate simultaneously the main factors which affect moisture transport.

SHELF-LIFE PREDICTION OF COMPOSITE READY-TO-EAT FOODS MATERIALS INCLUDING EDIBLE FILMS OR COATINGS

To assess edible moisture barrier performance more realistically than through WVP, D_{eff} or moisture sorption measurements, experimental moisture migration studies can be carried out in model composite food products. An experimental system which is as close as possible to the conditions that are encountered in the final food product, must be adopted. Some examples of experimental systems reported in the literature are presented below (Fig. 3) and the results of these experiments are summarized in Table 7.

These trials involve long and specific experimental studies which have to be repeated each time one parameter of the system (a_w difference, temperature of storage, or film thickness) is modified. Hence, predictive moisture migration models, validated with moisture migration experiments, constitute promising tools to speed up the development of composite food products with the desired properties.

Modelling Moisture Transfer in Multi-Components Food

Feasible mathematical models for prediction of mass transfer through coated food systems are usually based on Fickian models that were first developed to describe mass transfer in uncoated foods or in foods packaged with synthetic films (Rumsey and Krochta, 1994). These models can be classified in terms of increasing complexity with regard to the hypothesis, boundary, and limit conditions considered. This typology of models is reported in Table 8 and almost coincides with the chronological order of model development. Indeed, the generalization of
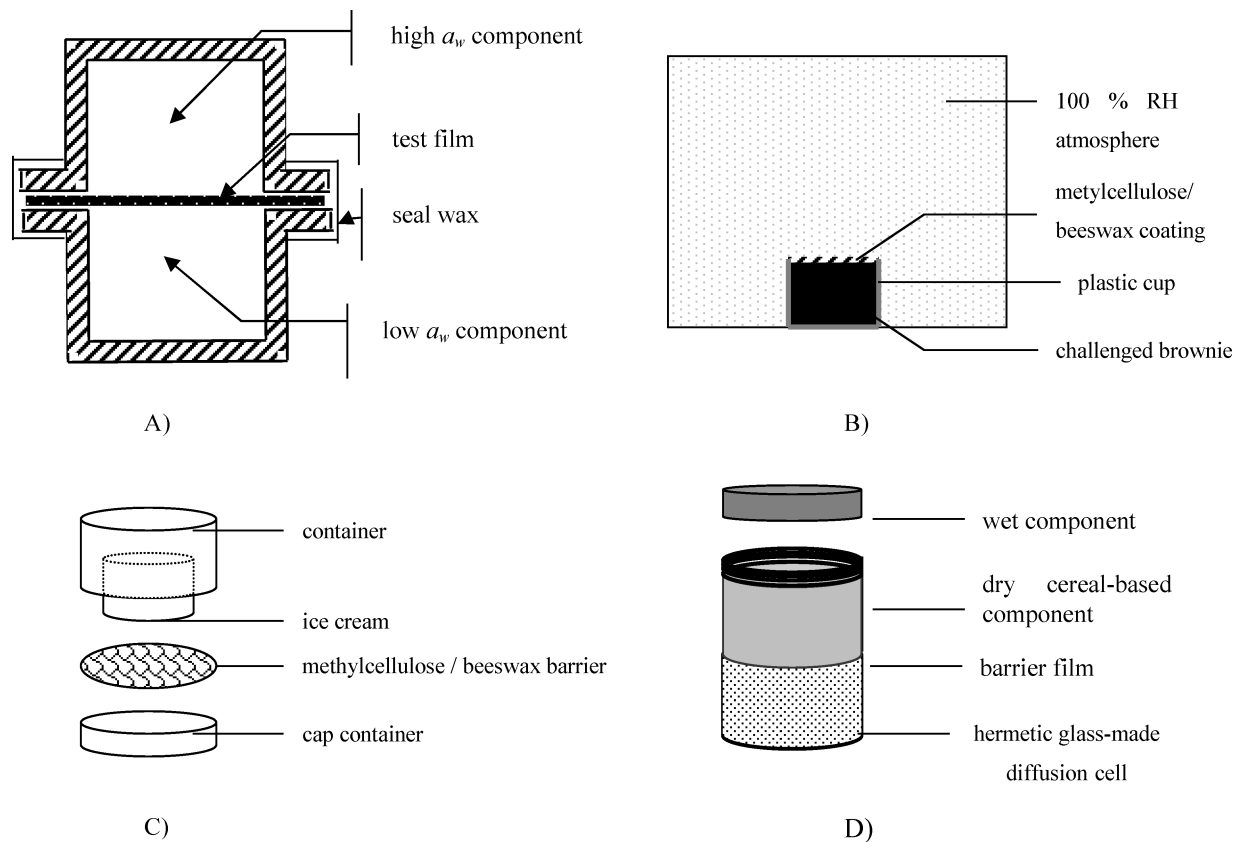
Figure 3 Comparison of schematic model composite food systems used to assess the performance of edible barrier; A) Schematic diagram of container used by Kamper and Fennema (1985) to test edible films as barrier at the interface between cracker and tomato paste; B) Schematic diagram of experimental set to test a emulsionned-based/beeswax edible barrier applied on the surface of a brownie (Greener and Fennema, 1989); C) Schematic diagram of containers to simulate a sundae ice cream cone and test methylcellulose/palmitic acid based films as moisture barrier (Rico-Pena and Torres, 1990); D) Schematic diagram of glass cells used to assess moisture transfer in three-component model foods (Guillard, 2003).

powerful programming tools favored the use of numerical solutions to solve the systems of equations describing transport mechanisms. These numerical solutions allowed considering more realistic hypothesis concerning the model food than when only analytical solutions were used.

The first models (type a) considered a steady-state regime of transfer in the barrier film, absence of internal resistance to transfer of the other component of the model food, linearized isotherms in the model food component, and barrier film. These simple assumptions were progressively abandoned to establish more realistic models which will be commented upon in the following section.

A model was first proposed by Karel and Labuza (1969) to estimate the gain or loss of moisture of a food held in a semi-permeable packaging or coating. These authors proposed integration over a given period of time, for constant external temperature and RH, of the equation (20) which is a mass balance equation derived under the hypothesis of pseudo-steady state conditions of moisture transfer through a coating:

$$\frac{dC_w}{dt} = WV_{Permeance} \cdot A(pe - p) \tag{20}$$

where dC_w/dt is the rate of moisture transferred per second, $WV_{Permeance}$ is the film permeance to moisture [g/s.m^2.Pa], A is the effective area of diffusion [m^2], p is the water vapour partial pressure in the coating and p_e the water vapour partial pressure in the environment [Pa].

Using a linear approximation of the food isotherm (Fig. 4), permits deducing equation (21) from equation (20):

$$\ln\left(\frac{C_{we} - C_{wi}}{C_{we} - C_{wc}}\right) = \frac{P.A.po.t}{x.M.bs} \tag{21}$$

where C_{we}, C_{wi} and C_{wc} are respectively the equilibrium, initial and critical moisture content in the coated food product [g/g d.b.]; P, the WVP of the coating [g.(m.s.Pa)$^{-1}$]; A the surface of contact [m^2]; po the saturating vapor pressure at the considered temperature [Pa]; x, the thickness of the coating; M, the dry weight of the packaged product [g d.b.]; bs [g/g d.b.] the slope of the packaged product linearized moisture sorption isotherm between the initial and critical a$_w$.

This linear model has been widely used and validated with experimental data for synthetic polymeric packaging (Bell and Labuza, 2000; Taoukis et al., 1988). However, although

Table 7 Summary of moisture migration experiments reported in literature to assess efficacy of lipid-based or multi-component edible films at reducing water transfer in multi-component food

Components/RH difference between components	Barrier composition thickness	CMC*	Shelf-life (hours)		References
			Ø barrier	With barrier	
Cracker (0.10 a_w)/tomato paste (0.86 a_w at 25°C, 0.82 a_w at 5°C)	Emulsion Methylcellulose/blend stearic – palmitic acids. (∼ 35 μm)	0.39 a_w in cracker	≈ 24 (25°, 5°) 504(−20°C)	504 (25°C) 840 (5°C) > 1680 (−20°C)	(Kamper et al., 1985)
Freeze-dried agar microcrystaline cellulose gels (0.30 a_w/0.85 a_w)	Dark chocolate (601 μm)	∼ 9g/100 g d.b, 0.4 a_w	2	1200 (−20°)	(Biquet et al., 1988)
Ice cream cones/ice cream	Methylcellulose: palmitic acid/chocolate/55–65 μm	"sogginess of cone"	2160 (−20°C)	No moisture uptake until 672 (−12°C); 1680 (−23°C)	(Rico-Pena et al., 1990)
Sponge cake (0.84 a_w)/Agar gel (0.99 a_w)	ACETEM 70 (293 μm) self-supported film/Aceto-monopalmitin (300 μm)	30 g/100 g (w.b) ∼ 0.87 a_w	6	216 (20°C)	(Guillard et al. 2003)
Dry biscuit (0.18 a_w)/Agar gel (0.99 a_w)	Acetomonopalmitine (316 μm)	10 g/100 g (w.b), 0.7 a_w	24 < 1	360 (5°C) 72 (??)	(Guillard et al., 2004c)
Baked pizza bottom (∼0.9 a_w) /starch gel (0.99 a_w)	Sprayed (Zein/ lauric acid/oil/Magnesium stearate)	0.97 a_w in the pizza bottom	< 24 (10°C)	Not reached after 600 hours (a_w ∼0.93)	(Plijter-schuddemat et al., 2003)
Coffee cookie (0.24)/custard cream	Brushed (Zein/stearic acid/soy fat/Magnesium stearate)	0.50 a_w	∼ 22(20°)	∼ 46	
Cracker (0.05 a_w)/RH of 65%	Emulsified films: corn starch, Methyl cellulose and soya oil (sprayed 30 μm)	8.25 g/ 100 g (d.b).	27	42 (20°)	(Bravin et al., 2005)
Cracker (0.05 a_w)/RH of 75%		∼ 0.33a_w	12	32	
Cracker (0.05 a_w)/RH of 85%			10	21	

*CMC: Critical Moisture Content considered in the cereal-based component which corresponds to the end of shelf life.

Table 8 Typology of models reported in literature to predict moisture transfer in composite model food including edible films

Type of models		State of the transfer	Diffusivity	Moisture sorption	Condition at interface	References
Model a	Barrier film	Steady state	RL and constant	Linearized	Instantaneous equilibrium of a_w	(Karel and Labuza, 1969)
	Other component(s)	Not considered	NRL, >>D_{eff} barrier			
Model b	Barrier film	Transient	RL and constant	Linearized		(Rumsey and Krochta, 1994)
	Other component(s)	Not considered	NRL >>D_{eff} barrier			
Model c	Barrier film	Steady state	constant	Linearized		(Hong et al., 1986; Hong et al., 1991)
	Other component(s)	Transient	constant	Linearized		
Model d	Barrier film	Transient	Constant in lipidic film/variable in hydrophilic films	Fitted with the Ferro Fontan model		(Guillard et al., 2003)
	Other component(s)		Variable			

frequently used to assess the efficacy of edible coatings in food products, it has been scarcely validated in such systems (Biquet and Labuza, 1988; Debeaufort et al., 1999; Debeaufort et al., 2002). Biquet and Labuza (1988) validated this model in composite systems protected by edible coatings based on:

- A mono-component system consisting of a 0.33 freeze dried agar/microcrystalline cellulose gel separated by a dark chocolate film from a 80% RH atmosphere.
- A bi-component system consisting of two freeze dried agar/microcrystalline cellulose gels preconditioned at 0.33 and 0.85 a_w separated again by a dark chocolate film.

After determining the permeability of the dark chocolate, moisture isotherms, and the diffusivity of the components, these authors supposed that the chocolate could be considered as the controlling resistance for moisture transfer. These authors applied equation (21) in the two systems along with a mass conservation in the bicomponent system.
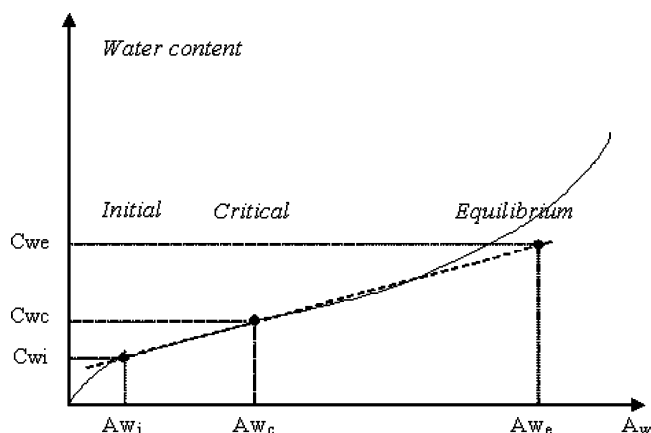
However, several assumptions limited the versatility of the previous model (type a):

(i) The linearization of the food isotherm was only valid on a narrow range of a_w. Integration of equation 21 using other models of moisture isotherm for the coated product is possible but requires the use of numerical integration. Such integration when the Guggenheim-Anderson-De-Boer equation is used is detailed in Touakis et al. (1988).

(ii) Equilibrium of vapor pressure between the coating and the food was assumed to be reached and moisture transfer in the coating to be in the steady state. This steady state means that the concentration gradient of moisture within the membrane remains unchanged and the rate of appearance of vapor on the outflow side is constant. Thus, the barrier film could not accumulate moisture as it is generally occurring during the early stage of migration.

(iii) The film was the rate limiting component for the moisture transfer, and consequently the internal resistance of the food product was negligible.

These assumptions do not always coincide with conditions that prevail in real food products. Rumsey and Krochta (1994)
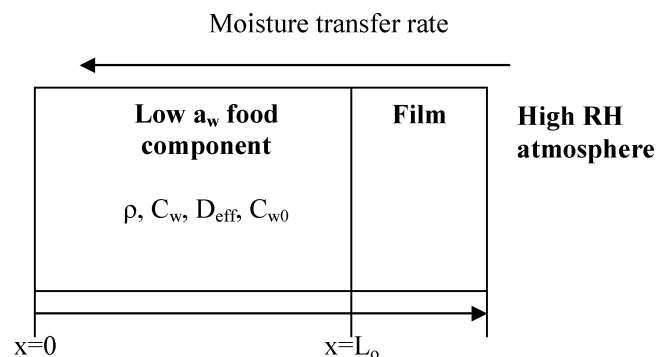

Figure 4 Linearization of the coated food component used in model a (Adapted from Karel and Labuza, 1969). With Cw_i, Cw_e, and Cw_c, respectively the initial, equilibrium, and critical moisture content after which the protected food component is considered as unacceptable.

Figure 5 Schema of the bi-component model food modelled by Hong et al. (model c, 1991). With x the spatial coordinate and ρ the apparent density, C_w the moisture content, D_{eff} the moisture diffusivity, and C_{w0} the initial moisture content of the food component.

abandoned assumption ii) and fitted the data obtained by Biquet and Labuza (1988) with poor results (model b). These authors still considered a constant moisture D_{eff} coefficient in the barrier film, while from the discussions of section on Testing procedures to Determine Water Vapor Permeability, one can conclude that the diffusion coefficient in a solid dispersion including hydrohilic compounds such as dark chocolate varies with moisture content. Taoukis et al. (1988) challenged assumption iii) and determined a criterion to compare the relative importance of the product internal resistance and the coating resistance. To do so, these authors calculated the ratio between the internal permeance of the food ϕ_{int} and the external permeance ϕ_{ext} (or k/x) of the coating:

$$\frac{\phi_{int}}{\phi_{ext}} \approx 2.5 \cdot \frac{\beta D/Lo}{WV_{Permeance}} \tag{22}$$

Where β_D is the permeability of the food [g/m/Pa], L_o the half thickness of the coating [m], $WV\,Permeance$ the permeance of the film [m²/s].

A dimensionless number, called the L number (L#) was defined as:

$$L\# = \frac{\beta_D/Lo}{WV_{Permeance}} \tag{23}$$

Assuming that if $\phi_{int} > 20\,\phi_{ext}$ the effect of internal resistance in the food was negligible, a rule was proposed by Taoukis et al. (1988): If $L_\# > 4$, the film is the major resistance and model a can be used; if $L_\# < 0.2$, the resistance of the food product had to be taken into account and model a cannot be applied. Hong et al. (1991) abandoned the assumption of uniform moisture in the food material (model c). The food product examined was a dried banana chip coated with various materials. Their model was still considered one-dimensional migration (Fig. 5) and was derived from Fick's Second Law:

$$\frac{\partial C_w}{\partial t} = D_{eff} \cdot \frac{\partial^2 C_w}{\partial x^2} \tag{24}$$

where the initial and boundary conditions are:

$$C_w(x, t) = C_{w0} \text{ at } t = 0; \quad 0 \le x \le Lo \tag{25}$$

$$\frac{\partial C_w}{\partial x} = 0 \text{ at } x = 0 \tag{26}$$

$$\rho\left(D_{eff} \cdot \frac{\partial C_w}{\partial x}\right) = WV_{Permeance}(pi - pe) \text{ at } x = L_o \tag{27}$$

where x is the spatial coordinate, C_w the moisture content of the coated food, ρ the apparent density of the coated food, D_{eff} moisture diffusivity of the coated food, pi and pe are respectively the water vapour pressure at the interface of the coating and the food, and in the environment of storage,

A program using the Crank-Nicolson finite difference method was used to solve equation (16) with the boundary conditions previously exposed.

Guillard et al. (2003) were the first authors to propose and validate a predictive model based on Fick's second law which took into account the internal resistance to transfer of each component in a composite food system including edible films (model d). The composite food system (high a_w component/barrier/low a_w component) was assumed to be composed of three finite plane sheets placed side by side (Fig. 6). This geometry limited strongly the interest of the model since there are only few cases where a real system can be reduced to three adjacent slabs. The equations governing moisture transfer in this system are detailed hereafter (Equations 28 to 30, case of constant D_{eff} in the components). The model could take into account either a variable or a constant effective diffusivity as a function of moisture content in the components which where determined from moisture migration experiments.

$$\frac{\partial C_{w1}}{\partial t} = D_{eff1} \frac{\partial^2 C_{w1}}{\partial x^2} \quad \text{for } -e_1 < x < 0 \tag{28}$$

$$\frac{\partial C_{w2}}{\partial t} = D_{eff2} \frac{\partial^2 C_{w2}}{\partial x^2} \quad \text{for } 0 < x < e_2 \tag{29}$$
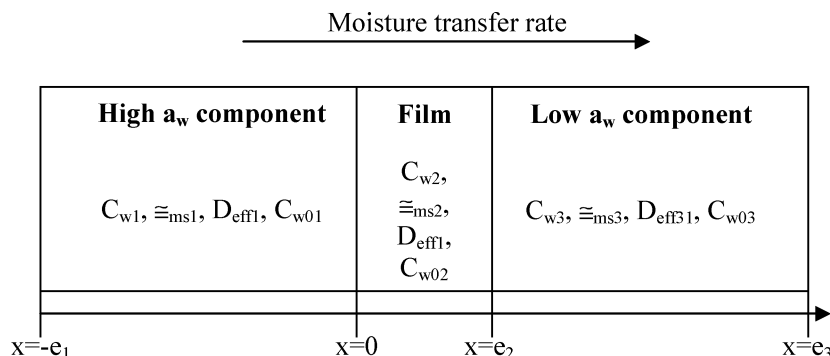

Figure 6 Schema of the three-component model food used by Guillard et al. (model d, 2003). With x the spatial coordinate and ρ_{msi} the apparent density, C_{wi} the moisture content, D_{effi} the moisture diffusivity, and C_{w0i} the initial moisture content of component i.

$$\frac{\partial C_{w3}}{\partial t} = D_{eff3} \; \frac{\partial^2 C_{w3}}{\partial x^2} \quad \text{for } e_2 < x < e_3 \qquad (30)$$

where x is the spatial coordinate, C_{wi} the moisture content in the component i, D_{effi} the moisture-effective diffusivity in the component i.

The model initial and boundary conditions were:

  (i) All components are initially at a uniform concentration $(C_{wi})_0$
 (ii) Water activity equilibrium is assumed to be reached instantaneously at the interface between components
 (iii) Mass conservation
 (iiii) No moisture gradient exists at the end of the wet (x = $-e_1$) and the dry (x = e_3) components

The finite-difference method of Crank-Nicholson was used to solve numerically the system of equations governing mass transfers in the food system.

Model Performance and Shelf-Life Predictions

The last generation of model (type d) were tested in several model foods. They presented accurate fittings which allowed determining extension of the period of acceptability for composite food including barrier films of variable compositions. In a three-component model food (sponge-cake/barrier film/agar gel), acetylated monoglycerides (Acetylation Degree ranging from 30 to 70%) permitted the best limitation of moisture transfer and higher performance than dark chocolate or gluten films. Acetyated monoglyceride barriers (100 μm thick) allowed to delay between 8 and 20 days the increase of sponge-cake moisture content (from 23 to 40% w. b.), which was reached in less than 2

days otherwise. The model was also used to compare the effect of fat addition in various components of the model food (Roca et al., 2005). Fat was added either in the dry component (fatty sponge cake), or in the wet component (processed cheese or fatty gelatine gel) or at the interface between components (acetylated monoglycerides layer). These authors concluded that the last configuration (continuous fat layer of 100 μm at the interface) was more favorable than the addition in the wet component. Considering a critical a_w of 0.92 in the sponge cake, this configuration corresponded to a 30 days period of acceptability compared to a few days in the other configurations. From a nutritional point of view, this last configuration also corresponded to the most limited addition of fat in the product (1 g/g w.b. of fat-free sponge cake). Bourlieu et al. (2006) validated the model on the range of intermediary a_w in various model systems (dry biscuit/hydrophobic barrier film/intermediary a_w wet component) with wet components that presented important internal resistance to moisture transfer. In these systems, using an extremely sensitive dry component, acetylated barriers, white beeswax, and blends of these two compounds, allowed significant extension of the period of acceptability: from a few hours up to 15 days using $\sim$300 μm self-supported barrier film. Once again, the barrier resistance was more important than the internal resistance of the wet components, even when these latters included large amount of a_w lowering agent in their formulation. However, the internal resistance of model food wet component has to be considered to estimate accurately the product period of acceptability. This influence was well illustrated by Roca et al. (2005) when comparing simulation obtained with model d or with the simplified model a (Fig. 7). Model d appeared to be more precise on the shelf-life prediction whereas model a led to an overestimation of the shelf-life because of too simplified assumptions.

Model d was also used to predict the influence of intrinsic (technology of formation of the coating) and extrinsic (storage temperature) factors on moisture transfer in model food
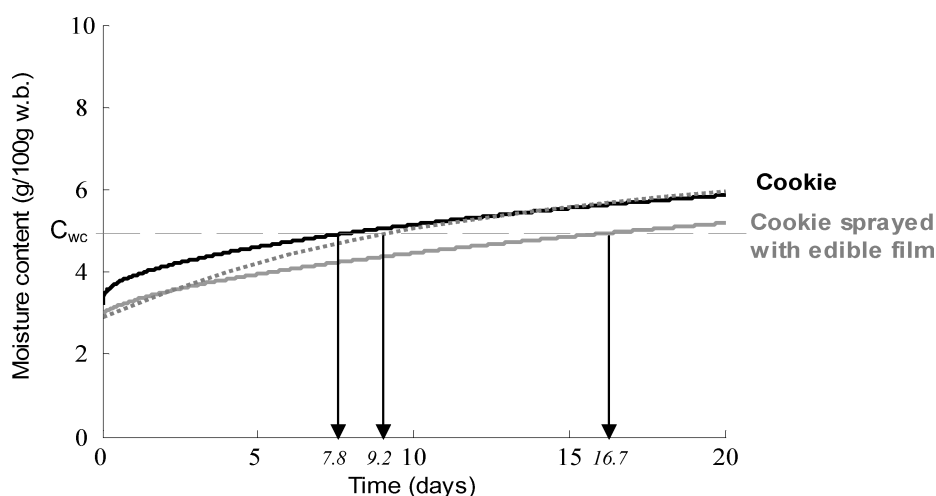

Figure 7 Prediction of the effect of applying an edible film on a multidomain food product shelf-life using model d (continuous lines) or model a (dotted line): predicted moisture content evolution with time for a cookie without and with an edible film sprayed on it surface, in direct contact with jam of initial a_w 0.70 (courtesy of Roca et al., 2005). With C_{wc} the critical moisture content after which the cookie is considered as unacceptable.

Table 9 Effect of temperature on moisture transfer in a two-component model food composed of a sponge-cake - $a_{wi} = 0.84$, 20°C - and agar gel - $a_{wi} = 0.99$, 20°C- (Guillard et al., 2004b)

	Model Food component	At 5°C	At 20°C	At 35°C
Effect of temperature on moisture Sorption	Agar gel ($a_{wi} = 0.99$, 20°C)		No significant difference over a 0.95–1 a_w range	
	AMG barriers		Increasing water sorption with increasing temperature	
	ACETEM 50	MC = 1.32 g/100 g a_w = 0.75	MC = 1.51 g/100 g a_w = 0.75	MC = 2.15 g/100 g a_w = 0.75
	AMP	MC = 0.82	MC = 1.37	Above Melting point (30°C)
		$a_w = 0.75$	$a_w = 0.75$	
	Sponge-cake		No significant difference, tendency of increased sorption with increasing temperature over a 0–1 a_w range	
Effect of temperature on moisture Diffusivity (D_{eff})	Agar gel ($a_{wi} = 0.99$, 20°C)		Non-rate limiting, not investigated	
	ACETEM 50	$D_{eff} = 0.9 \times 10^{-11}$ m²/s	$D_{eff} = 1.9 \times 10^{-11}$ m²/s $E_a = 43.7$ KJ/mole	$D_{eff} = 5.7 \times 10^{-11}$ m²/s
	AMP	$D_{eff} = 1.9 \times 10^{-11}$ m²/s	$D_{eff} = 2.1 \times 10^{-11}$ m²/s	
	Sponge-cake	$E_a = 39.2 X^{-0.11}$ KJ/mole, from to 27.6 to 0.1 × 10^{-10} m²/s for a_w varying from 0.7 to 1	E_a varying from 35.5 to 47 KJ/mole on all the range of water activity from 31.8 to 0.3 × 10^{-10} m²/s for a_w varying from 0.7 to 1	from 220.6 to 0.5 × 10^{-10} m²/s for a_w varying from 0.7 to 1
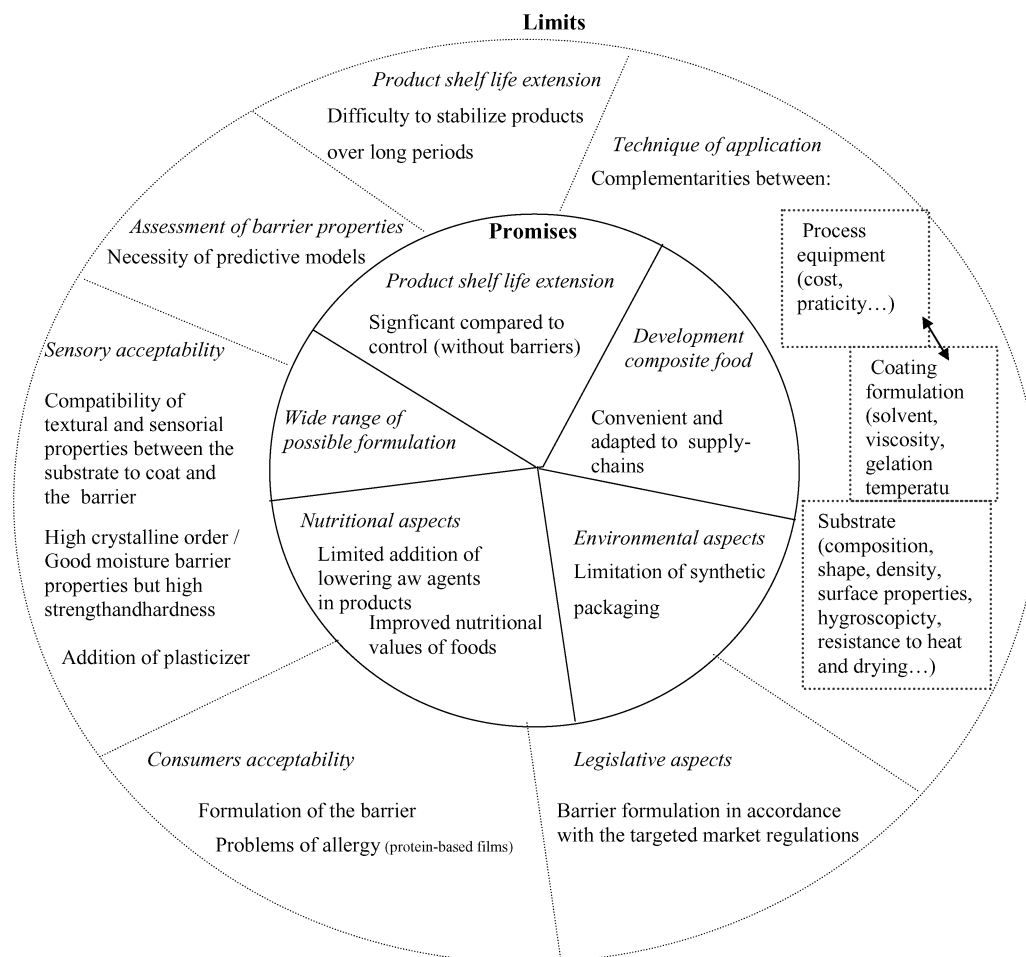
Figure 8 Promises and limits of edible moisture barriers (adapted from Bourlieu et al., 2007).

including coating. Guillard et al.(2004b) investigated the effect of variation of storage temperature (T = 5°C, 20°C, and 35°C) on the water transfer in a model food product composed of a sponge-cake (a_{wi} = 0.84, 20°C) and an agar gel (a_{wi} = 0.99, 20°C) separated by acetylated monoglyceride barriers. A summary of the work is presented in Table 9 which casts light on the drastic effect of temperature increase on moisture transfer and variable of sensitivity of fat barriers to this parameter in relation with its composition.

CONCLUSIONS AND FUTURE TRENDS

A wide range of edible moisture barriers has been explored in 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 in complement of naturally present protective layers, is now generalized. Edible moisture barriers including lipids or inert fillers present an important potential in term of stabilization of composite food products over prolonged period of time and reduction of fat or sugar addition. Edible barriers seem to present an interesting answer to the demand of consumers for higher quality and long-shelf-life products, while reducing disposable packaging material and increasing recyclability. The large list of edible film ingredients available allows targeting a wider range of potential functional properties. Most reviews on edible film pointed out that the best edible film for a given application was the one presenting the better adequation with the food product (similar ingredients, compatibility and the like), with its condition of storage and primary mode of deterioration. On a sensory point of view, inorganic coatings seem attractive but their compatibility with the product and acceptability by consumers could be limited.

If an enlarged choice of edible film constituents is now possibly, a realistic assessment of the film barrier properties is probably the major hurdle to their application in processed food. Assessment of edible film barrier properties has been mainly based on WVP measurements of self-supported structures. These measurements, though allowing relative classifications of barrier materials present several drawbacks: i) they hardly describe the conditions of use, storage of the barrier; ii) they are based on abusive assumptions (no interactions with water, linearized moisture sorption isotherm); iii) despite standard procedures, variable testing conditions have been reported (water activity difference, temperature, and state of materials). Several formal or mechanistic models have been proposed to describe the influence of testing conditions on the barrier properties of edible films. However, most of them were only validated on a narrow range of conditions. Few empiric attempts of determination of performance of edible films in real food products have also been reported. These methods are usually destructive and laborious and have to be repeated for each targeted application.

Only few original predictive models based on Fick's second law have been used to assess shelf-life extension of composite food products achieved using barriers in real conditions of use. With the development of powerful programming tools and numerical solutions of equations, these models take into account more and more complex hypothesis. The models are used to describe water diffusion mechanism in various barrier matrixes, considering concentration-dependent diffusivities, complex type II isotherm, resistance at interface, possible retraction/swelling of material and effect of temperature abuse. These models also facilitate an integrative approach needed to abide by all the requirements (regulations, sensorial, nutritional, and technical) to use a barrier film in a food product (Fig. 8). On the other hand, complex models, closer to realistic conditions, reinforce the need of precise input parameters and high speed methods of data collection, for validation on a wide range of external conditions. Non destructive methods of moisture content determination (MRI, spectrometry) should offer favorable answer to these needs. In addition, these methods allow monitoring microscopic changes in water concentration. This should lead to a better understanding of the mechanism of transfer, possibilities of non-Fickian contributions, and evolution of the molecular architecture of the edible material during the transfer. Indeed the success of formal models to represent macroscopic transport is far from proving their validity on a mechanistic or theoretical point of view.

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