



Prolongation of the Shelf-life of Perishable Food Products using Biodegradable Films and Coatings

Stéphane Guilbert, Nathalie Gontard and Leon G. M. Gorris*

S. Guilbert: Ecole Nationale Supérieure Agronomique de Montpellier, 2 Place P. Viale, F-34060 Montpellier (France)

N. Gontard: CIRAD-SAR/ENSIA-SIARC, 73 Rue J.F. Breton, BP 5035, F-34000 Montpellier (France)

L.G.M. Gorris: Agrotechnological Research Institute (ATO-DLO), Bornsesteeg 59, P.O. Box 17, NL-6700 AA Wageningen (The Netherlands)

The improvement of the safety and quality of minimally processed foods is of major interest to both the consumer and the food industry and is the topic of an EU-sponsored research project with nine international partners. The project optimizes existing techniques and in addition develops novel technologies to ensure high quality and safe food products. Among the systems studied is Modified Atmosphere Packaging, for which the available packaging film materials are tailored to the specific demands of the food products. A novelty in the project is the development of biodegradable packaging materials that can replace conventional synthetic materials. Additionally, edible coatings that are applied directly on the food surface are designed which create a modified atmosphere. The edible coatings can be furnished with active compounds such as antimicrobials or antioxidants to obtain additional desired effects. Such packagings and coatings may protect very powerfully against microbial spoilage and loss of intrinsic product quality, resulting in a prolonged shelf-life. An overview of the development and application of edible films and coatings is given here, comprising recent results from the EU project with regard to the barrier properties of edible films and the inclusion of active compounds.

©1996 Academic Press Limited

Introduction

The increased consumer demand for high quality, long shelf-life, ready-to-eat foods has initiated the development of only mildly preserved products that keep their natural and fresh appearance as far as possible. An extensive range of ready-to-eat foods is available, comprising raw and minimally processed (washed, trimmed, sliced) vegetables and Sous Vide preparations (cooked vegetable and potato based dishes). With financial support from the EU, a group of seven research institutions and two convenience food-manufacturers has set out to come to a practical application of optimal mild preservation techniques, amongst others (combinations of) refrigeration, modified atmosphere packaging (MAP) and bioconservation, that can prolong shelf-life without severely (extensively) affecting the fresh-like quality of the products.

An important aspect in this research project (AIR1-0125) is the design and application of biodegradable (edible) coatings and packaging materials suitable for fresh or minimally processed fruits and vegetables. In general, edible coatings can be applied directly to the surface of a food product as an additional hurdle for protection of overall food quality and stability. The functional characteristics required for the coating depend on the product matrix (low to high moisture

content) and the deterioration processes the product is subject to. Films made of such biodegradable material can also be employed as packaging materials to generate a suitable modified atmosphere around a packaged product and might replace non-biodegradable plastics used in MAP storage today.

Proteins, lipids and polysaccharides are the main constituent of edible films and coatings. Their presence and abundance determines the barrier properties of the material with regard to water vapour, oxygen, carbon dioxide and lipid transfer in food systems. Potential applications and properties of edible films have been reviewed in detail elsewhere (1-4). A brief account is given here of the development of edible films and coatings and the specific challenges met in their application with high moisture food products.

Edible Films and Coatings History

The concept of employing edible films as protective coatings for foods is not at all novel, the earliest documented uses being in the 1800s (5). Patents on edible films to extend the shelf-life of foods date back to the 1950s, comprising films for frozen meat, poultry and sea-food using alginates, fats, gums and starches (6-9). Waxes have also been employed for a long time to coat fruits and vegetables in order to limit physiological deterioration processes and microbial spoilage

*To whom correspondence should be addressed.

and to control gas exchange (10–12). The application of edible films with processed foods, especially those characterized by a high moisture content, is an area that has received little attention.

An edible coating is a thin film prepared from edible material that acts as a barrier to the external elements (factors like moisture, oil, vapour) and thus protects the product and extends its shelf-life. Examples of some food coatings are wax for fresh fruits and vegetables, shellac coatings on candies and nuts, natural casings on meat products, and gelatin capsules for pharmaceuticals. The major benefit of the edible coatings is that they can be consumed along with the food, can provide additional nutrients, may enhance sensory characteristics and may include quality-enhancing antimicrobials. Because they may be consumed, the composition of edible films or coatings must conform to the regulations that apply to the food product concerned. The interest in the development of biodegradable and edible packagings is also increasing due to environmental concerns and regulations.

Biopolymer films and coatings are generally designed using biological materials such as polysaccharides, polyester proteins, lipids and derivatives. Natural biopolymers have the advantage over synthetic biopolymers that they are biodegradable and renewable raw materials. They can be used effectively to make biodegradable coatings and packagings to replace short shelf-life plastics. Films primarily composed of polysaccharides (cellulose and derivatives, starch and derivatives, gums, etc.) or proteins (gelatin, zein, gluten, etc.) have suitable overall mechanical and optical properties, but are highly sensitive to moisture and show poor water vapour barrier properties. In contrast, films composed of lipids (waxes, lipids or derivatives) or polyesters (poly-D- β -hydroxybutyrate, polylactic acid, etc.) have good water vapour barrier properties, but are usually opaque and relatively inflexible. Lipid films could be also quite fragile and unstable (rancidity). Starch is the most commonly used natural biopolymer, since it is inexpensive, widely available and relatively easy to handle. Other types of biopolymers such as cellulose, lipids and vegetable proteins have been investigated, e.g. cellulose/polyurethane mixtures (13), gluten/synthetic resin mixtures (14), vegetable protein/vinyl compound mixtures (15), and casein or lipid/synthetic polymer mixtures (16).

Films may consist of single or multiple components, are dry or moist, single or bilayer, etc. However, the foods to be coated or packaged differ in many biochemical and physical aspects (moisture content, pH, matrix polarity, etc.). Many of the films developed to date are dry films of layered structures that are very well suited to protect dry to intermediate moisture food products. However, most existing films are not suited for high moisture food products (foods with high surface water activity) because they swell, dissolve or disintegrate upon contact with water (2).

Krochta and co-workers recently designed milk-protein based coatings, mainly consisting of caseinate and lipids, specifically suited for minimally processed vege-

tables (17–19). Some successful applications include the use of 14 to 16 g/kg sodium caseinate/1–2 g/kg stearic acid to coat peeled carrots stored at 2.5°C (70% RH; air speed 20 cm³/min). The coating eliminated white blush formation and decreased dehydration dramatically (18). Coating uncut celery sticks with caseinate/acetylated monoglyceride resulted in a 75% reduction in moisture loss at 2.5°C and 70% RH (19). Industrial applications of films prepared from protein substances include the use of collagen in sausage casings, corn zein for protective wrapping films and caseinates and whey proteins in a vast range of food and non-food products (20).

Driven by the awareness that care should be taken not to exhaust the world's natural resources and to deteriorate the environment by using non-degradable and non-recyclable materials, this development has for the best part been focused on edible film-forming biopolymers, which typically allow full recycling and are completely biodegradable within a considerably short period of time. Where edibility remains throughout the process of film production, there is an enormous potential for the application of natural biopolymers as the packaging materials and coatings of the future generation. A tremendous new market could be opened for both traditional and novel agricultural crops which are the source of the desired film-forming biopolymers.

Coating and Film Manufacture

Coatings are applied and formed directly on the food product, whereas films are structures which are applied after being formed separately. They can be superficial coatings or continuous layers between compartments of the same food product. The simple or mixed use of different carbohydrate, protein or lipid materials in various forms (coatings, single-layer, bilayer or multi-layer films), has been proposed for the manufacture of edible films and coatings that have controlled barrier properties and are suited for high moisture foods. Edible films and coatings can be formed by the following mechanisms (21):

Simple coacervation: where a hydrocolloid dispersed in water is precipitated or undergoes a phase change after solvent evaporation (drying), after the addition of a hydrosoluble non-electrolyte in which the hydrocolloid is insoluble (e.g. ethanol), after pH adjustment of the addition of an electrolyte which induced salting out or cross-linking.

Complex coacervation: where two hydrocolloid solutions with opposite electron charges are mixed, thus causing interaction and precipitation of the polymer complex.

Gelation or thermal coagulation: where heating of the macromolecule, which leads to its denaturation, is followed by gelatin (e.g. proteins such as ovalbumin) or precipitation, or even cooling of a

hydrocolloid dispersion causing gelation (e.g. gelatin or agar).

Free, self-supporting films can be obtained by standard techniques, e.g. extrusion, moulding or rolling mill procedures, which have been developed for non-edible films. Films (or packaging material) are most commonly formed by drying a film-forming solution on a drum dryer, thermoforming (of pulp to make ice-cream cones, French fries and convenience food containers, etc.) or hot extrusion (for thermoplastic biopolymers).

Film-forming Properties

Edible and biodegradable films must meet a number of specific functional requirements (moisture barrier, solute and/or gas barrier, water or lipid solubility, colour and appearance, mechanical and rheological characteristics, non-toxicity, etc.). These properties are dependent on the type of material used, its formation and application. Plasticizers, cross-linking agents, antimicrobials, antioxidants, texture agents, etc. can be added to enhance the functional properties of the film. In any polymeric packaging film or coating, two sets of forces are involved: between the film-forming polymer molecules for all polymeric films or coatings (cohesion), and between the film and the substrate for coatings only (adhesion). The degree of cohesion affects film properties such as resistance, flexibility, permeability, etc. Strong cohesion reduces flexibility, gas and solute barrier properties and increases porosity (22). Cohesion depends on the biopolymer structure and chemistry, the fabrication procedure and parameters (temperature, pressure, solvent type and dilution, application technique, solvent evaporation technique, etc.), the presence of plasticizers and cross-linking additives and on the final thickness of the film. Film cohesion is favoured by high chain order polymers. Excessive solvent evaporation or cooling, which is generally required for industrial reasons, may sometimes produce non-cohesive films due to premature immobilization of the polymer molecule.

The film-forming properties of wheat gluten films have been extensively studied by Gontard *et al.* (21–23). Within EU project AIR1-0125, hydrophilic films with good resistance to breakage and abrasion properties and with appropriate flexibility have been realized on the basis of wheat gluten and pectin. The dependence of the film development on pH and on polymer and ethanol concentration has been established. More hydrophobic, composite and multilayered films have been obtained using film-forming solutions containing pectin and beeswax. Reviews of the film-forming properties of films based on other polysaccharides, proteins or lipids can be found elsewhere (1,4,24).

Barrier Properties

The moisture barrier properties of edible films have

been studied by many research groups. In many cases it was found that inclusion of lipid compounds reduced moisture transport (25–28). Studies have focused on films containing lipids, which are less permeable, or proteins, which are more permeable. Protein-containing films would thus have feasible applications with high moisture foods, such as (processed) fresh fruits and vegetables. The water vapour transmission strongly depends on temperature, prevailing relative humidity on either barrier side and hydratability of the barrier. It is, therefore, paramount that studies on moisture barrier properties of films give adequate reference to these conditions. In compliance with this, Koelsch and Labuza (29) published an extensive list of edible films containing lipid compounds, specifically stating the temperature and relative humidities at which the permeabilities were assessed. Water vapour permeability for protein films have been determined mostly in single sets of temperature and relative humidity (RH) gradient conditions. For example, water vapour permeability values have been reported for soy protein isolate films at 25°C and 100–50% RH gradient (30) and for wheat gluten films at 21°C and 0–85% RH gradient (31), 30°C and 0–100% RH gradient (21) and 23°C and 0–11% RH gradient (32). Recently, water vapour transmission test results at 10% RH gradients and three different temperatures (5, 30 and 50°C) were presented for wheat gluten films (22).

The gaseous barrier properties of edible films have been studied only quite recently, especially in relation to temperature (30,33–35). Results obtained in the AIR1-0125 project have shown that RH has a strong influence on the transmission rates of oxygen and carbon dioxide. For a given wheat gluten film, it was observed that oxygen permeability increases slowly from 0.24 to 1.5 mL.m/(m².d.atm) going from 0–60% RH (25°C) and showed an exponential rise up to 200 mL.m/(m².d.atm) at 91% RH. A similar steep increase in permeability was observed for carbon dioxide, going from < 10 mL.mm/(m².d.atm) at 60% RH to 6000 mL.mm/(m².d.atm) at 91% RH (25°C). The selectivity of the film towards O₂ and CO₂, expressed as the ratio of CO₂ permeability over O₂ permeability, increased from 4–6 at 60% RH to 28.4 at 94.5% RH, implying that the films gradually became more permeable to CO₂ relative to O₂ (36). These sharp increases could be correlated to modifications in the protein network structure and polymer mobility within the film, corresponding to changes from a glassy to a visco-elastic state at higher RH. A similar behaviour has been observed with films made from other hydrophilic biopolymers such as cellophane, ethylene-polyvinyl alcohol and MC-palmitic acid. **Table 1** gives an overview of the gas barrier properties of a range of edible and synthetic films in order to illustrate the influence of the film composition. At higher RH values, edible films were found to have higher oxygen and carbon dioxide permeabilities than synthetic films. The addition of lipid components (beeswax, DATEM) to wheat gluten based films caused a marked decrease in permeabilities. This decrease may be related to a reduction in the water

Table 1 Oxygen and carbon dioxide permeabilities of edible and synthetic films at 25°C

Film type	Oxygen permeability pO ₂ mL.mm/(m ² .d.atm)	Carbon dioxide permeability pCO ₂ mL.mm/(m ² .d.atm)	Film selectivity (pCO ₂ /pO ₂)	Relative humidity (%)
Pectin	57.5	—	—	87
Pectin	258.8	4132	16	96
Chitosan	91.4	1553	17	93
Pullulane	3.3	14	4.24	30
Pullulane/arabic gum	3.05	10	3.27	36
(Wheat) gluten	190	4750	25	91
(Wheat) gluten	250	7100	28.4	94.5
Fish proteins	56	—	—	86
Fish proteins	169	2156	12.75	92
Na caseinate	77	462	6	77
Gluten-DATEM	153	1705	11.14	94.5
Gluten-Beeswax	133	1282	9.64	91
Na caseinate/Myvacet	83	154	1.85	48
MC/HPMC/fatty acids	46.6	180	3.86	52
MC and beeswax (bilayer)	4	27	6.75	42
Gluten-DATEM and beeswax (bilayer)	<3	15	>5	56
Gluten-Beeswax and beeswax (bilayer)	<3	13	>5	56
PET ^a	1	—	—	100
Ethylene/Polyvinyl alcohol ^a	4	—	—	100
Polyamide 6	9.8	—	—	100
Oriented polypropylene ^a	44	—	—	100
Cellophane ^b	55	—	—	100
Methylcellulose-palmitic acid ^c	78.8	—	—	100

^aMichel and Vandenaël (47); ^bRigg (48); ^cRico-Pena and Torres (34); others: AIR1-0125 and Gontard *et al.* (36).

Abbreviations: AM: acetylated monoglycerides; DATEM: diacetylated tartaric ester of monoglycerids; HPMC: hydroxypropyl-methylcellulose; MC: methylcellulose.

content of the film due to the presence of the hydrophobic substances or a strengthening of the protein structural matrix by the lipids whereby the barrier properties are altered. It has been found that the permeability of edible films towards O₂ can be very low, even as to create anaerobic conditions on the food surface (28,35). When anaerobiosis occurs, anaerobic pathogens such as *Clostridium botulinum* could become a hazard. Inclusion of an antimicrobial compound, e.g. sorbic acid, would then be advised to control this organism.

The ability of films to modify gas transport is important for tailoring such films to specific applications such as fresh fruit and vegetables, which are characterized by active metabolism even during refrigerated storage. Coatings or films applied to such respiring products should allow for the right modification of the gaseous environment inside the package, i.e. allowing O₂ to penetrate into the package and excessive CO₂ to escape from it (37). Both wheat gluten and soy protein isolate films have been shown to be very effective oxygen barriers (30,33) at low relative humidity, whereas their vapour barrier ability is rather limited.

Mechanical Properties

Films must be generally resistant to breakage and abrasion (to strengthen the structure of a food filling, to protect it) and flexible (in order to adapt to possible

deformation of the filling without breaking). The mechanical properties of edible films and coatings depend on the type of film-forming material and especially on its structural cohesion. Cohesion is the result of a polymer's ability to form strong and/or numerous molecular bonds between polymeric chains, thus hindering their separation. This ability depends on the structure of the polymer and especially its molecular strength, geometry, molecular weight distribution and the type of position of its lateral groups. The mechanical properties are also linked with the film-forming conditions, e.g. type of process and solvent, cooling or evaporation rate, etc., and the coating technique (spraying, spreading, etc.). The puncture strength of gluten films is strongly dependent on the gluten concentration and pH of the film-forming solution (21). A resistant film can be obtained by using a film-forming solution with high gluten content (125 g/kg) at about pH 5.

The mechanical properties of biodegradable packaging made from synthetic polymer/starch mixtures depend on the starch content, compatibility (between hydrophobic synthetic polymers and hydrophilic starches) and treatments to enhance this parameter, for instance by addition of compatibilization agents. For first generation packaging, increasing the percentage of starch reduces puncture strength and extensibility (38).

The mechanical properties of amorphous materials are seriously modified when temperatures of these compounds rise above the glass transition temperature (T_g).

The glass transition phenomenon separates materials into two domains according to clear structural and property differences, thus dictating their potential applications. Below T_g the material is rigid, and above it becomes visco-elastic or even liquid. Indeed, below this critical threshold only weak, uncooperative local vibration and rotation movements are possible. Film relaxation relative to temperature follows an Arrhenius time course. Above the T_g threshold, strong, cooperative movement of whole molecules and polymer segments can be observed. These are cooperative structural rearrangement movements.

Optical properties of biopolymeric film depend on the film formulation and fabrication procedure, e.g. opacity of wheat gluten films is highly dependent on film-forming conditions (21). Opacity of low density polyethylene/starch films increases as starch concentration and granule diameter increase (37).

Retention of Additives

Films and coatings can help to maintain desirable food quality characteristics such as colour, flavour, spiciness, acidity, sweetness, saltiness, etc. (1). Some commercial films, for instance pullulane-based films are thus available in several colours, or with spices and seasonings (39). Enriching coatings with functional additives allows improvement of nutritional and aesthetic quality aspects without destroying the integrity of the food product.

Growth of microorganisms on the surface of packaged food products is the predominant cause of spoilage, which may be counter-acted using antimicrobial compounds. With many refrigerated foods, which are often subject to changes in temperature, condensation of water inside the package increases surface moisture, thus promoting spoilage. Loss of colour, desired flavour or texture and generation of off-flavours are among the physiological and chemical deterioration processes that lower product quality (36). Edible coatings are conducive to the use of antimicrobials and antioxidants. In fact, inclusion of these compounds in coatings concentrates them at the produce surface which is the place where protection is needed. This means that only very small amounts of additives are required.

Quite a number of compounds with good forming properties, such as proteins, polysaccharides, lipids and resins, are often listed as food additives. A summary of additives differing in functionality and approved use with foods is given in **Table 2**. With regard to the inclusion of active compounds into edible films and coatings, Guilbert (40) discussed the use of casein or carnauba wax films with sorbic acid to protect papaya and apricot cubes from spoilage by yeasts and fungi, which is a problem at product water activities over 0.78. Also, retention of the antioxidant tocopherol in gelatin films was studied for application with margarine. It was found that cross-linking the gelatin was necessary to retard sufficiently the migration of the highly-fat soluble tocopherol into the margarine. Others found

Table 2 Food additives with different functionality (extracted from (49))

Functionality	Food additive	GRAS/GMP ^a status
Antimicrobial agent	Sodium benzoate	+
	Benzoic acid	+
	Propionic acid	+
	Potassium sorbate	+
	Sorbic acid	+
Antioxidant	Ascorbic acid	+
	Ascorbyl palmitate	+
	Butylated hydroxyanisole	+
	Butylated hydroxytoluene	+
	Citric acid	+
	Propyl gallate	+
	Tocopherols	+
Coating components	Calcium chloride (firming agent)	+
	Glycerol (plasticizer)	+
	Polyethylene glycol (binder, plasticizer)	-
	Propylene glycol (plasticizer)	-
	Silicone (release agent)	-
	Sorbitol (plasticizer)	-

^aGRAS: Generally Recognized As Safe; GMP: Good Manufacturing Practice.

that edible films composed of pectinate, pectate or zein that contained citric acid were very useful to prevent rancidity and maintain desirable texture of nuts. The inclusion of nisin, a bacteriocin produced by certain strains of *Lactococcus lactis* that suppresses *Listeria monocytogenes* (41) or bacteriocins from other sources that may control nonproteolytic strains of *Clostridium botulinum*, in edible films is currently studied in EU project AIR1-0125. Both pathogens are able to grow at low temperature and low oxygen tension in minimally processed vegetables packaged under modified atmospheres (37).

Considerable research effort has been devoted to the migration of additives from coatings into the food. This is a determinative factor, both in terms of activity and impact on desired food quality. Sorbic acid has been a kind of model additive in migration studies (42–45). It is increasingly being used as one of the numerous preservative hurdles employed in intermediate moisture foods, low pH foods, or shelf-stable products (42). It is important to be able to predict and control sorbic acid migration between phases during: (a) food treatments (e.g. absorption of sorbic acid during the processing of dried prunes, or loss during cooking of fabricated foods); (b) storage of composite foods (e.g. dairy products or cakes containing pretreated fruits); (c) storage of foods in contact with wrapping materials or films containing sorbic acid (absorption by dairy products covered with paper saturated with sorbic acid); and (d) storage of foods coated with an external edible layer highly concentrated in sorbic acid.

Guilbert and co-workers studied the migration of potassium sorbate and sorbic acid from pectin, gluten and composite films in model food systems within the framework of AIR1-0125. They observed a marked dependence of the migration of potassium sorbate from a film in relation to the initial sorbic acid concentration,

the pH and the temperature, as is illustrated in **Fig. 1** for a pectin film. **Table 3** compares the diffusion coefficient of sorbic acid with several other edible films reported in literature. The diffusion coefficient for sorbic acid from a wheat gluten-glycerol film into a model food was found to be 9×10^{-12} at 20°C. Addition of lipid components such as DATEM and AM or the more hydrophobic beeswax resulted in a 50% reduction of the diffusivity, and thus caused active retention of sorbic acid. These values are about

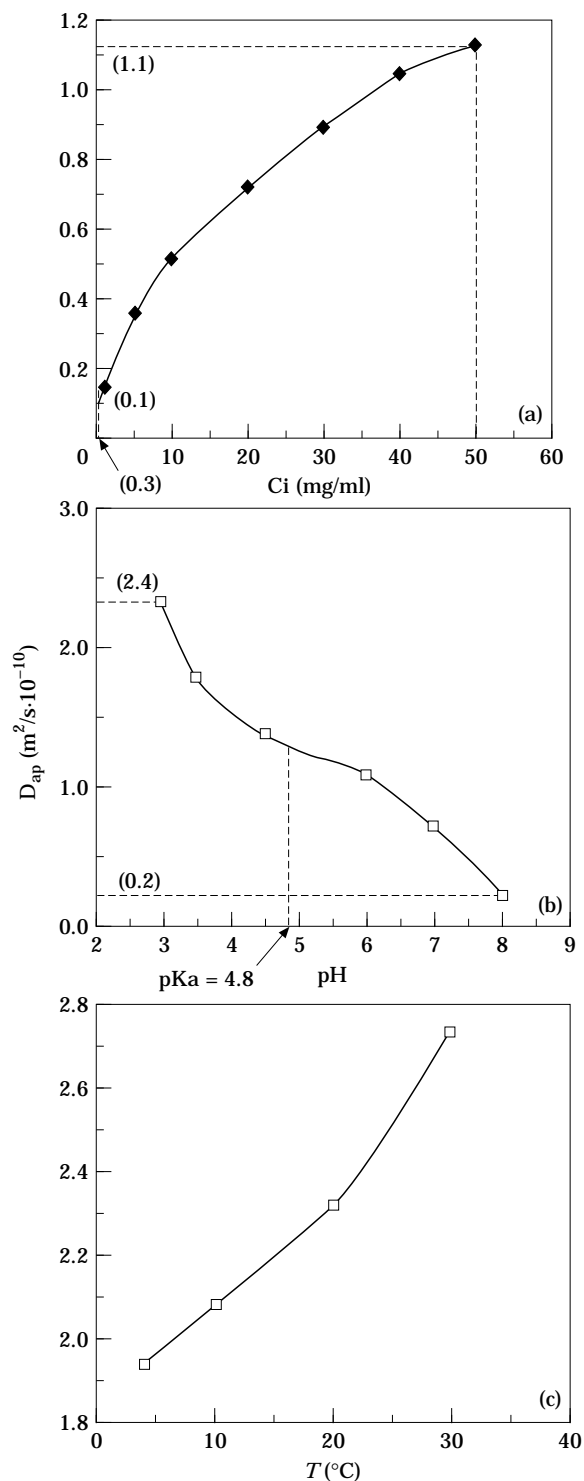


Fig. 1 Retention of K-sorbate in a pectin film, in relation to (a) concentration of K-sorbate in the film, (b) pH, and (c) temperature (52)

Table 3 Diffusion coefficient of sorbic acid in a model food system and in edible films

Film composition	Diffusion coefficient ($D=10^{-12}\text{m}^2/\text{s}$)	Temperature ($^{\circ}\text{C}$)
Cheese analog ^a	100	24
Agar gel and glycerol ^b	350	24
Wheat gluten (glycerol)	9	20
Hydroxypropyl-methylcellulose ^c	8.3	24
Chitosan ^c	8.7	24
Gluten-DATEM 20% w/w	6.4	20
Gluten-DATEM 30% w/w	4.6	20
Gluten-AM 20% w/w	4.7	20
Gluten-AM 30% w/w	4.9	20
Gluten-Beeswax 20% w/w	5.2	20
Gluten-Beeswax 30% w/w	6.2	20
Methylcellulose	3.3	24
Zein ^a	0.33	24
HPMC-palmitic acid 25% ^c	2	24
MC-palmitic acid 25% ^c	1.2	24
AM 100%	0.27	20
Beeswax 100%	0.0007	20

^aTorres *et al.* (45); ^bGiannakopoulos and Guilbert (50); ^cVojdani and Torres (46,51); others: AIR1-0125.

Abbreviations: AM: acetylated monoglycerides; DATEM: diacetylated tartaric ester of monoglycerides; HPMC: hydroxypropyl-methylcellulose; MC: methylcellulose.

equivalent to those found in literature for films based on chitosan, cellulose derivatives and lipids. Films prepared from lipid compounds only (MA and beeswax) showed even lower migration. With high moisture foods, these lipid films would be most advantageously used as a monolayer film or as a bilayer film composed of a hydrophilic base layer coated with a thin layer of lipid containing sorbic acid.

Conclusion

The use of edible films and coatings for a wide range of food products, including fresh and minimally processed vegetables and fruits, receives increasing interest because it improves on product shelf-life, may add to the texture and sensory characteristics, and is environmentally friendly. Edible films, coatings and biodegradable packagings produced from biological materials offer numerous advantages over other conventional synthetic packaging materials. Their application relates to their function as internal moisture or solute barriers with heterogeneous foods, individual protection of food pieces, encapsulation of functional food additives, etc. It may be evident from the above discussion that specific film types allow for specific applications. Films with low water barrier properties would thus be more suitable for foods with a high moisture content and a long shelf-life. While at present, a wealth of information has been gathered on the physical and chemical properties of edible films and coatings, matching the various properties of edible films to the specific characteristics of food products is one of the main challenges for the near future.

References

- 1 KESTER, J.J. AND FENNEMA, O.R. Edible films and coatings: a review. *Food Technology*, **40** (12), 47–59 (1986)
- 2 GUILBERT, S. Technology and application of edible protective film. In: MATATHOULHI, M. (Ed), *Food Packaging and Preservation*. New York: Elsevier Applied Science Publishers, pp. 371–394 (1986)
- 3 CUQ, B., GONTARD, N. AND GUILBERT, S. Edible films and coatings as active layers. In: ROONEY, M. (Ed), *Active Food Packaging*. Blackie Academic and Professional, pp. 111–142 (1994)
- 4 KOELSCH, C. Edible water vapor barriers: properties and promise. *Trends in Food Science & Technology*, **5**, 76–80 (1994)
- 5 ALLEN, L., NELSON, A.I., STEINBERG, M.P. AND MCGILL, J.N. Edible corn-carbohydrate food coatings. II. Evaluation of fresh meat products. *Food Technology*, **17** (11), 104–108 (1963)
- 6 BAUER, C.D., NEUSER, G.L. AND PINKALLA, H.A. *U.S. patent 3,406,081* (1968)
- 7 EARLE, R.D. *U.S. patent 3,395,024* (1968)
- 8 EARLE, R.D. AND SNYDER, C.E. *U.S. patent 3,255,021* (1966)
- 9 SHAW, C.P., SECRIST, J.L. AND TUOMY, J.M. *U.S. patent 4,196,219* (1980)
- 10 MACK, W.B. AND JANER, J.R. Effects of waxing on certain physiological processes of cucumbers under different storage conditions. *Food Research*, **7**, 38–47 (1942)
- 11 KRAGHT, A.J. Waxing peaches with the consumer in mind. *Produce Marketing*, **9**, 20–21 (1966)
- 12 WAKS, J.M., SCHIFFMAN-NADEL, M., LOMANIEC, E. AND CHALUTZ, E. Relation between fruit waxing and development of rots in citrus fruit during storage. *Plant Disease*, **69**, 869–870 (1985)
- 13 MUELLER, H.P., TILLMAN, H. AND GUNTER, W. *European patent EP449041 A2* (1991)
- 14 ARANYI, C., GUTFREUND, K., HAWRYLEWICZ, E.J. AND WALL, J.S. *U.S. patent 3,522,197* (1970)
- 15 FRIEDMAN, M. In: POMERANZ, Y. (Ed), *Industrial Uses of Cereals* Symposium Proceedings A.A.C.C., pp. 237–251 (1973)
- 16 ROBEY, M.J., FIELD, G. AND STYZINSKI, M. Degradable plastics. *Materials Forum*, **13**, 1–10 (1989)
- 17 KROCHTA, J.M., PAVLATH, A.E. AND GOODMAN, N. Edible films from casein-lipid emulsions for lightly-processed fruits and vegetables. In: *Proceedings of the 5th ICEF Congress*, Cologne, p. 56 (1989)
- 18 AVENA-BUSTILLOS, R.J., CISNEROS-ZEVALLOS, L.A., KROCHTA, J.M. AND SALVEIT, M.E., JR. Optimization of edible coatings on minimally processed carrot to reduce while blush using response surface methodology. *Transactions ASAE*, **36**, 801–805 (1993)
- 19 AVENA-BUSTILLOS, R.J., KROCHTA, J.M. AND SALVEIT, M.E. Optimization of caseinate-based edible coatings on 'Red Delicious' and celery sticks. *Journal of the American Horticultural Society*, in press (1995)
- 20 KINSELLA, J.E. Milk proteins: physio-chemical and functional properties. *CRC Critical reviews in Food Science and Nutrition*, **21**, 197–262 (1984)
- 21 GONTARD, N., GUILBERT, S. AND CUQ, J.L. Edible wheat gluten films: influence of main process variables on films properties using response surface methodology. *Journal of Food Science*, **57**, 190–199 (1992)
- 22 GONTARD, N., GUILBERT, S. AND CUQ, J.L. Water and glycerol as plasticizers affect mechanical and water vapor barrier properties of an edible wheat gluten film. *Journal of Food Science*, **58**, 206–211 (1993)
- 23 GONTARD, N., DUCHEZ, C., CUQ, J.L. AND GUILBERT, S. Edible composite films of wheat gluten and lipids: water vapor permeability and other functional properties. *International Journal of Food Science and Technology*, **29**, 39–50 (1994)
- 24 MCHUGH, T.H. AND KROCHTA, J.M. Milk-protein based edible films and coatings. *Food Technology*, **48**, 97–103 (1994)
- 25 HAGENMAIER, R.D. AND SHAW, P.E. Moisture permeability of edible films made with fatty acids and (hydroxypropyl)-methylcellulose. *Agriculture Food Chemistry*, **38**, 1799–1803 (1990)
- 26 HAGENMAIER, R.D. AND SHAW, P.E. Permeance of shellac coatings. *Agriculture Food Chemistry*, **39**, 825–829 (1991)
- 27 KESTER, J.J. AND FENNEMA, O. Resistance of lipid films to water vapor transmission. *Journal of the American Oil Chemists*, **66**, 1139–1146 (1989)
- 28 KESTER, J.J. AND FENNEMA, O. The influence of polymorphic form on oxygen and water vapor transmission through lipid films. *Journal of the American Oil Chemists*, **66**, 1147–1153 (1989)
- 29 KOELSCH, C.M. AND LABUZA, T.P. Functional, physical and morphological properties of methylcellulose and fatty acid-based edible barriers. *Lebensmittel-Wissenschaft und -Technologie*, **25**, 404–411 (1992)
- 30 BRANDENBURG, A.H., WELLER, C.L. AND TESTIN, R.F. Edible films and coatings from soy protein. *Journal of Food Science*, **58**, 1086–1089 (1993)
- 31 PARK, H.J. AND CHINNAN, M.S. Properties of edible coatings for fruits and vegetables. ASAE paper No. 90-6510, ASAE St. Joseph, MI (1990)
- 32 GENNADIOS, A. AND WELLER, C.L. Edible films and coatings from soymilk and soy protein. *Cereal Foods World*, **36**, 1004–1009 (1991)
- 33 GENNADIOS, A., WELLER, C.L. AND TESTIN, R.F. Temperature effect on oxygen permeability of highly permeable, hydrophilic edible films. *Journal of Food Science*, **58**, 212–214, 219 (1993)
- 34 PICO-PENA, D.C. AND TORRES, J.A. Oxygen transmission of an edible methylcellulose-palmitic acid film. *Journal of Food Processing and Engineering*, **13**, 125–133 (1990)
- 35 KESTER, J.J. AND FENNEMA, O.R. Temperature influence on oxygen and water vapor transmission through stearyl alcohol films. *Journal of the American Oil Chemistry Society*, **66**, 1154–1157 (1989)
- 36 GONTARD, N., THIBAUT, R., CUQ, J.L. AND GUILBERT, S. Influence of relative humidity and film composition on oxygen and carbon dioxide permeabilities of edible films. *Journal of Agricultural and Food Chemistry* (in press)
- 37 GORRIS, L.G.M. AND PEPPELENBOS, H.W. Modified atmosphere and vacuum packaging to extend the shelf-life of respiring food products. *HortTechnology*, **2**, 303–309 (1992)
- 38 LIM, S.T., JANE, J.L., RAJAGOPALAN, S. AND SEIB, P.A. Effect of starch granule size on physical properties of starch filled polyethylene film. *Biotechnology Progress*, **8**, 51–57 (1992)
- 39 HANNIGAN, K. Edible plastic. *Food Engineering*, **March**, 98–99 (1984)
- 40 GUILBERT, S. Use of superficial edible layer to protect intermediate moisture foods: application to the protection of tropical fruit dehydrated by osmosis. In: SEOW, C.C. (Ed), *Food Preservation by Moisture Control*. London: Elsevier Applied Science Publishers, pp. 199–220 (1988)
- 41 GORRIS, L.G.M. AND BENNIK, M.H.J. Bacteriocins for food preservation. *ZFL*, **45**, 65–71 (1994)
- 42 LEISTNER, L. In: GOULD, G.W. (Ed), *New Methods of Food Preservation*. Glasgow: Blackie Academic and Professional, pp. 1–21 (1995)
- 43 GIANNAKOPOULOS, A. AND GUILBERT, S. Sorbic acid diffusivity in relation to the composition of high and intermediate moisture model gels and foods. *Journal of Food Technology*, **21**, 477–485 (1986)
- 44 GUILBERT, S., GIANNAKOPOULOS, A. AND CHEFTEL, J.C. Diffusivity of sorbic acid in food gels at high and intermediate water activities. In: SIMATOS, D. AND MUL-

- TON, J.L. (Eds), *Properties of Water in Relation to Food Quality and Stability*. Dordrecht: Martinus Nijhoff Publishers, pp. 343-356 (1985)
- 45 TORRES, J.A., MOTOKI, M. AND KAREL, M. Microbial stabilization of intermediate moisture food surfaces. I. Control of surface preservative concentration. *Journal of Food Processing and Preservation*, **9**, 75-79 (1985)
- 46 VOJDANI, F. AND TORRES, J.A. Potassium sorbate permeability of methylcellulose and hydroxypropyl methylcellulose coating: effect of fatty acids. *Journal of Food Science*, **55**, 841-846 (1990)
- 47 MICHEL, C. AND VANDENAEL, Y. *Food Packaging*, Vol. 2. Intensive Erasmus course, 15-21 September 1991, University of Gent, Gent, Belgium
- 48 RIGG, W.J. Measurement of the permeability of chilled meat packaging film under conditions of high humidity. *Journal of Food Technology*, **14**, 149-155 (1979)
- 49 CUPPETT, S.L. Edible coatings as carriers of food additives, fungicides and natural antagonists. In: KROCHTA, J.M., BALDWIN, E.A. AND NISPEROS-CARRIEDO, M.O. (Eds), *Edible Coatings and Films to Improve Food Quality*. Lancaster, U.S.A.: Technomic Publishing Co, pp. 121-137 (1994)
- 50 GIANNAKOPOULOS, A. AND GUILBERT, S. Determination of sorbic acid diffusivity in model food gels. *Journal of Food Technology*, **21**, 339-353 (1986)
- 51 VOJDANI, F. AND TORRES, J.A. Potassium sorbate permeability of polysaccharide films: chitosan, methylcellulose and hydroxypropyl methylcellulose. *Journal of Food Process Engineering*, **12**, 33-48 (1989)
- 52 DE SAVOYE, F., DALLE ORE, F., GONTARD, N. AND GUILBERT, S. Improvement of fresh fruits and vegetables shelf-life and quality: surface retention of preservative agents using edible films and coatings. In: International colloque 'Le Froid et la qualité des légumes frais', 7-9 September 1994, Brest, France (1994)