

## **BIO-PACKAGING: TECHNOLOGY AND PROPERTIES OF EDIBLE AND/OR BIODEGRADABLE MATERIAL OF AGRICULTURAL ORIGIN**

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### **Abstract**

Edible films, coatings and biodegradable packagings produced from biological materials offer numerous advantages over other conventional synthetic packaging materials. Potential applications of edible films are numerous (internal moisture or solute barriers of heterogeneous foods, individual protection of food pieces, encapsulation of food additives etc...). Advantages, types, formation and properties of edible films with examples are reviewed in detail. Biodegradable packaging, made from entirely renewable natural polymers could contribute to solving environmental pollution and creating new markets for agricultural products. Different approaches are discussed (physical mixing of starch or co-processing of more than 50% starch with synthetic polymers, thermoplastic extruded starch etc...)

## INTRODUCTION

Formulations of packaging films, food or pharmaceutical coatings etc... must include at least one component able to form an adequately cohesive and continuous matrix. These components are macromolecules that are either synthetic, from which most current packaging is produced, or natural biopolymers. The performances and applications of synthetic packaging are fully controlled and utilized, whereas the two ends of the production line (raw materials and the fate of the packaging after use) are not. Environmental problems can thus result from using non-renewable raw materials and accumulation of such non-biodegradable packaging. As a solution to this dilemma, biopolymers could be used to formulate biodegradable packaging, e.g. to replace short shelf life plastics, in addition to adoption of plastic recycling programs. These biopolymers can be classified in four general categories: polyosides, proteins, lipids and polyesters (obtained by controlled vegetal or bacterial biosynthesis). Films primarily composed of polyosides (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 vapor barrier properties. In contrast, films composed of lipids (waxes, lipids or derivatives) or polyesters (poly-D- $\beta$ -hydroxybutyrate, polylactic acid etc...) have good water vapor barrier properties, but are usually opaque and relatively inflexible. Lipid films could be also quite fragile and unstable (rancidity).

Three different techniques using agricultural raw materials (fully renewable raw materials) to make bio-packaging are proposed (Fig. 1): synthetic polymer/biopolymer mixtures (first and second generations), agricultural materials used as fermentation substrates to produce microbial polymers and finally agricultural polymers used directly as basic packaging material.

Starch is the most commonly used agricultural raw material, especially in the first two techniques, since it is inexpensive, widely available and relatively easy to handle.

## I- USE OF BIOPOLYMERS IN PACKAGING

### I-1- Synthetic polymer/biopolymer mixtures

Synthetic polymers become more susceptible to microbial attack when biopolymers are incorporated, i.e. biodegradability of the synthetic polymer is accelerated by adding components that can be assimilated by microorganisms. Presently, the main marketed products of this type are starch-based. Other types of biopolymers such as cellulose, lipids and vegetable proteins are not widely used and some have been investigated only

recently (e.g. cellulose/polyurethane mixtures<sup>95</sup>, gluten/synthetic resin mixtures<sup>6</sup>, vegetable protein/vinyl compound mixtures<sup>36</sup>, casein or lipid/synthetic polymer mixtures<sup>108</sup>).

### **I-1-1- Filled material (first generation)**

The first commercial "biodegradable" plastics were developed using a technique involving extrusion mixing of granular native starch (5-20%) and prooxidative and auto-oxidative additives with the synthetic polymer. This technique has been marketed by several firms: the St Lawrence Group (Canada) under the "Ecostar" trademark; Archer Daniels Midland (USA) as "Polyclean"; Polychim (France) as "Ecopolym", and Amylum as "Amyplast". Starch granules are uniformly dispersed in the polyethylene matrix without chemical interaction. Microbial enzyme-induced biodegradation of starch reduces the mechanical properties of the material and increase the interface between the polymer and the surrounding atmosphere (oxygen, water etc...). This stimulates profound chemical degradation (auto-oxidation) of the synthetic phase. Poor starch/polyethylene compatibility weakens the mechanical properties of the material, thus limiting the percentage of starch that can be added. This compatibility has been enhanced by silylation (increased hydrophobicity) of the surface of starch granules. The formed film can therefore contain up to 43% starch (St-Lawrence Corn Starch Company, Canada; Spartech, USA). Biodegradability of these materials is highly controversial<sup>125, 76, 77</sup>, and their behavior is now classified as "biofragmentation", i.e. fragmentation into small molecules. It takes 3-5 years to degrade this type of product into dust.

### **I-1-2- Composite material (second generation)**

A fine molecular mixture of synthetic polymers and starch-based polymers can be made by this technique. These materials are composed of gelatinized starch (up to 40-75%, by destructuring the starch granule with ammonia and water at high temperature), hydrophobic synthetic polymers (polyethylene etc...) and hydrophilic co-polymers. The latter compounds act as compatibility agents providing an interface between the starch and the synthetic polymer. Starch is thus not restricted to the dispersed phase, it is able to interact with the synthetic polymer. Compatibility agents can be synthetic (ethylene/acrylic acid, vinyl alcohol, or acrylic ester co-polymers, polyvinylalcohol, vinyl acetate...), or obtained by grafting polystyrene chains to amylose chains or amylopectin. These types of materials are marketed by: Ferruzzi (Italy), under the "Mater-Bi" trademark; Ampacet (USA), as "Poly-grade II" and Agri-Tech Industries (USA). Their prices (about 25 FF/kg for "Mater-bi") are still higher than that of standard synthetic packaging films ( 5 à 10 FF/kg for polyethylene or PVC). This aspect has been studied by Otey and Westhoff<sup>98, 100, 101, 102, 103</sup>, Lenk and Merrill<sup>83</sup>,

Bierman and Narayan<sup>14, 96, 97</sup>. Full biodegradability of these materials, as claimed by the manufacturers, is still a topic of discussion. Indeed, few standard, strictly-controlled, exhaustive comparative tests on biodegradability have been published. Complete degradation of starch takes 40 days and degradation of the entire film requires a minimum of 2-3 years, as compared to 200 years estimated for entirely synthetic polymers<sup>118</sup>.

### **I-2- Microbial polymers (polyester)**

Polyesters are theoretically biodegradable since ester linkages within polymer chains are potential targets of chemical or enzymatic (microbial) hydrolysis. Polyesters are excreted or stored by microorganisms. Starch hydrolysates are generally used as fermentation feedstock, for the microorganisms that produce polyesters. Isolation and purification costs are very high for these products that are obtained from complex mixtures. They are completely biodegradable<sup>76, 77</sup> and recyclable.

Le poly hydroxy butyrate/valérate (PHB/PHV), marketed under the "Biopol" trademark by ICI (UK), is produced by an *Alcaligenes eutrophus*. strain The sugar to polymer conversion yield is about 33%. It is thermoplastic and can be formed by the same techniques as those used for synthetic polymers. PHV or polycaprolacton are plasticizers which enhance PHB flexibility. This product is limited to use with products of high value (cosmetic, surgical products etc...) because of its relatively expensive (50-150 FF/kg).

Polylactic and polyglycolic acids are mainly produced by CCA Biochem (Netherlands) by chemical polymerization of lactic acid and glycolic acid obtained by *Lactobacillus* fermentation of carbohydrates (sucrose, glucose, maltose and lactose). Applications (surgical products) are extremely limited by the prohibitively high price (4000-20000 FF/kg).

Polycaprolactons and chitosans (combined with cellulose) are produced by Union Carbide (USA) as "Tone", and Aisero Chemical (Japan), but are only used to small extent in packaging materials.

### **I-3- Packaging composed of polymers of agricultural origin**

Films composed of polymers of agricultural origin (in a natural state or fractionated, e.g. whole grains, flours, proteins, starch, fractions...) are often much less sophisticated than the above described packaging. These products are economical due to the low cost of raw materials (3 FF/kg for starch, 4-5 FF/kg for gluten, as compared to 4-5 FF/kg for polyethylene as raw material). They are completely biodegradable, and edible when no non food-grade additives are used.

#### **I-3-1- Biodegradable packaging made from thermoplastic biopolymers**

"All-starch" packaging has been developed mainly by the Warner-Lambert Company (USA), under the "Novon" trademark, utilizing the thermoplastic properties of corn starch. The controlled presence of water or other plasticizers (glycerol, sorbitol ...) lowers the glass transition temperature of starch and films can be formed below the breakdown temperature (molecular degradation) of this polymer. Standard techniques used for forming synthetic polymer films can thus be used (extrusion, injection moulding). Fabrication costs are the same as for synthetic polymers.

This type of material can be used in relatively rigid packaging with a short shelf life (egg containers, fast food packaging), medical applications, non edible packaging and agricultural mulching.

Raw agricultural starch-based materials have been developed by Future Pop and Alexander Fruit & Trading Co. (USA), with foam starch chips replacing non-degradable polystyrene chips as filling material for packaging of shock sensitive goods. These starch chips cost 20% less than synthetic chips and are biodegradable.

Moreover, Biograna (Switzerland) and Tai'wan Sugu (Tai'wan) produce injection-molded dishware composed of various raw cereals devoid of other additives.

### **I-3-2- Edible packaging**

Edible films or coatings have long been used empirically to protect food products. A few examples of such applications to improve product appearance or conservation include sugar and chocolate coatings for candies, wax coating for fruits and traditional lipoprotein "skins" ("Yuba" obtained by drying the skin formed after boiling soya milk). Solid lipids and oils are also commonly used to cover or coat foods. Edible films are an interesting and often essential complementary parameter to control the quality and stability of many foods.

There are several reviews on the formulation technology and application of edible films <sup>50, 67, 79, 93</sup>. Certain basic aspects of the mechanisms and techniques for forming and applying films, coatings and microencapsulation are described in studies aimed at pharmaceutical applications <sup>8, 29, 75</sup>. The simple or mixed use of different glucide, protein or lipid materials in various forms (coatings, single-layer, bilayer or multilayer films), has thus been proposed for the formulation of edible films or coatings.

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. Edible films may be arbitrarily defined as thin layers of material which can be eaten by the consumer as part of the whole food product. The composition of edible films or coatings must therefore conform to the regulations that apply to the food product concerned.

Edible films and coatings can be formed by the following mechanisms <sup>67</sup>:

-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 or the addition of an electrolyte which induces 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.

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

Film coating materials such as waxes or lipids and derivatives can be applied either as a stable emulsion or micro-emulsion with water or by direct application while still melted <sup>48, 50, 67</sup>.

Direct application and distribution of the film coating material in a liquid form can be obtained by hand-spreading with a paint brush, spraying, falling film enrobing, dipping and subsequent dripping, distributing in a revolving pan (pan coating), bed fluidizing or air-brushing etc... <sup>67</sup>. Suitable food coating and adhesion, which is sometimes difficult to obtain when, for instance, hydrophobic materials are used to protect hydrophilic fillings (or vice versa), can be obtained by hot applications, coating the support with a surfactant or adding it to the film-forming solution. Another way is to apply a preparatory precoat with a material that can adhere to all filling components (e.g. starch precoat on raisins before a wax coating, or cocoa powder precoat on peanuts before a sugar coating).

Full descriptions of numerous industrial production lines are noted in some patents and in publications for raisin coatings <sup>86</sup>, for use of the commercial "Lepak" film-forming preparation <sup>21</sup>, for the application of starch films <sup>56</sup>, for the application of pectin films <sup>117</sup>, for coating ice-cream cones <sup>12</sup>, for coating fruit pieces <sup>113</sup>, for an compressed air spraying apparatus capable of homogeneously coating red variety meats <sup>106</sup> etc...

Free, self-supporting film 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 fry and convenience food containers etc...) or hot extrusion (for thermoplastic biopolymers).

## II - PROPERTIES AND APPLICATIONS OF "BIO-PACKAGING"

Edible and biodegradable films must meet with 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, anti-microbial, anti-oxygen agents, 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<sup>8</sup>. The degree of 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 favored 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 immobilisation of the polymer molecule.

## **II-1 Organoleptic properties**

Edible films and coatings must have organoleptic properties that are as neutral as possible (clear, transparent, odorless, tasteless etc.) so as not to be detected when eaten. Enhancement of the surface appearance (e.g. brilliance) and tactile characteristics (e.g. reduced stickiness) could be required. Hydrocolloid based films are generally more neutral than those formed from lipids or derivatives and waxes, which are often opaque, slippery and waxy tasting. It is possible to obtain materials with ideal organoleptic properties, but they must be compatible with the food filling, e.g. sugar coatings, chocolate layers (or imitation chocolate<sup>121, 122</sup>), and starch films for candies, biscuits, some cakes and ice-cream products (wafer coating), etc...

Films and coatings can also help to maintain desirable coloring, flavor, spiciness, acidity, sweetness, saltiness concentrations etc.<sup>50, 67</sup>. Some commercial films, especially Japanese pullulane-based films (marketed by Colorcon Ltd., under the "Opadry" trademark)<sup>52</sup>, are thus available in several colors, or with spices and seasonings. This procedure could be used to provide nutritional improvement without destroying the integrity of the food product (edible films and coatings enriched with vitamins and various nutrients).

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



<sup>38</sup> (Fig. 2). Opacity of low density polyethylene/starch films increases as starch concentration and granule diameter increase <sup>84</sup>.

## II-2 Mechanical properties

Films must be generally resistant to breakage and abrasion (to strengthen the structure of a food filling, to protect it, and ease handling) and flexible (enough plasticity 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 length, geometry, molecular weight distribution and the type and position of its lateral groups. The mechanical properties are also linked with the film-forming conditions (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 <sup>37, 38</sup>. A resistant film can therefore be obtained by using a film-forming solution with high gluten content (12.5%) at about pH 5 (Fig. 3).

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 (addition of compatibilization agents). For first generation packaging, increasing the percentage of starch reduces puncture strength and extensibility <sup>65, 84</sup>.

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 viscoelastic or even liquid. Indeed, below this critical threshold only weak, non-cooperative 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. In the  $T_g$  ( $T_g + 100^\circ\text{C}$ ) temperature range, these movements are given by the following equation of Williams, Landel & Ferry <sup>130</sup>:

$$\log a_T = C_1(T - T_g) / C_2 + (T - T_g)$$

where  $a_T$  represents the ratio between values for specific mechanical characteristics and temperatures  $T$  and  $T_g$  and  $C_1$  and  $C_2$  are constants whose values ( $C_1=17.4$  and  $C_2=51.6$ ) are virtually universal for a wide range of materials.



This glass transition phenomenon has been demonstrated in gluten films by differential scanning calorimetry and confirmed through dynamical, mechanical and thermal analysis by Gontard et al. <sup>42</sup>. The phenomenon seems to be a crucial physico-chemical parameter for understanding and predicting the behaviour of edible films such as that formed with gluten.

The mechanical properties of films can be enhanced by plasticization of the polymeric network. There are two different plastifying effects. Internal plasticization is obtained by modifying the chemical structure of the polymer, e.g. by co-polymerisation, selective hydrogenation or transesterification when edible lipid or derivative materials are used. External plasticization is obtained by adding agents which modify the organisation and energy involved in the tridimensional structure of film-forming polymers <sup>8</sup>. Reduction of the intermolecular forces between polymer chains, consequently the overall cohesion, facilitates extensibility of the film (less brittle, more pliable) and reduces its Tg. However, this also results in reducing the gas, vapor and solute barrier properties of the film <sup>8, 29, 80</sup>.

Another plasticization technique involves adding relatively inert solids (filling agents which reduce molecular exchange and cohesion of the final film). Particle sizes and distributions are important. Microcrystalline cellulose, various protein isolates and cocoa powders have thus been used as plasticizers, particularly for lipid films <sup>13, 34</sup>.

Water is the most common plastifier and is very difficult to control in biopolymers which are generally more or less hydrophilic. Plasticization of biopolymeric films is thus dependent on the usage conditions, especially relative humidity (of environment and packaged products). In isothermic conditions, the addition of plastifiers such as water has theoretically the same effect as increased temperature on molecular mobility.

Water causes a substantial drop in the Tg <sup>115</sup>. This effect has been demonstrated in gluten films <sup>39, 42</sup> and with other biopolymers such as elastin <sup>57</sup>, gelatin <sup>91</sup>, starch <sup>92, 131</sup>, hemicellulose and lignin <sup>66</sup> and with low molecular weight sugar <sup>17, 88, 107</sup>. This phenomenon could be utilized to reduce the glass transition temperature of biopolymers to below the decomposition temperature threshold. Standard techniques for synthetic polymer films such as extrusion or injection moulding, could thus be used. However, the drawback of this phenomenon is that it makes biopolymer packaging moisture-sensitive. Their mechanical properties are generally greatly modified by high temperature and/or moisture (ambient or from the packaged product) <sup>32, 39</sup>. Some treatments (especially the use of hydrophobic compounds such as octenyl succinate starch, oxidised polyethylene and fatty acids) are reported to reduce these negative effects <sup>32, 45, 55</sup>.

Standard techniques to evaluate the mechanical properties of packaging materials can be applied to "bio-packaging". Puncture strength, extensibility to puncture, torsion resistance, elasticity ... can be evaluated using texturometers and traction/compression testing equipment. However, edible films are more sensitive to ambient physical conditions, i.e. temperature and relative humidity, which must be carefully controlled.

### II-3 Water and lipid solubility

Solubility or insolubility in water or lipids could be required for films in some specific applications. Edible small bags or capsules <sup>27, 79, 46</sup> can be used to package premeasured portions of additives for potential dispersion in food mixtures (e.g. emulsifiers for the preparation of cake and bread batters) or for instant dried food preparations (e.g. individual drinks or soups).

Generally, most edible hydrocolloïd films and coatings are water soluble, unless a cross-linking or tanning treatment has been carried out or denaturing conditions are used. Gontard et al. <sup>38</sup> demonstrated the influence of film-forming conditions (pH and % ethanol) on water solubility of gluten films after 24 h immersion (Fig. 4).

When developing films that are effective moisture barriers under a broad range of relative humidities, it is often necessary to use materials that are almost or entirely insoluble in water so as to avoid loss of the film qualities through swelling or disintegration upon contact with the food <sup>50</sup>. In such instances, the use of lipids or almost insoluble proteins such as zein or gluten is recommended.

### II-4 Gas, solute, lipid and water vapor permeability

#### a- The permeability concept

Permeability is defined as a state which permits the transmission of permeants through materials <sup>89</sup>. When there are no pores, faults or membrane punctures, permeability (P) is equal to the product of the diffusion coefficient (D), representing the mobility of permeant molecules in the polymer, and of a solubility coefficient (S), representing the permeant concentration in the film in equilibrium with the external pressure:

$$P = D \cdot S$$

In practice, P is determined by steady state measurements:

$$P = \Delta W \cdot x / \Delta t \cdot A \cdot \Delta p$$

where  $\Delta W$  is the permeant weight that passes through a film of thickness  $x$  and area  $A$ ; and where  $t$  is the time and  $\Delta p$  the differential partial pressure across the film.

The diffusion coefficient can be obtained by taking measurements before the steady state is reached. The solubility coefficient can either be calculated from P and D, or measured in a separate experiment (sorption isotherms).

The diffusion and solubility of permeants are affected by temperature, and the size, shape and polarity of the diffused molecule. Moreover, these two parameters depend on film characteristics, including the type of forces influencing molecules of the film matrix, the degree of cross-linking between molecules, crystallinity, the presence of plasticizers or additives, etc... <sup>28, 39, 80, 111</sup>.

Permeability is only a general feature of films or coatings when  $D$  and  $S$  are not influenced by permeant content, thus when Fick's and Henry's laws apply. In practice, for most edible films the permeant interacts with the film and  $D$  and  $S$  are dependent on the differential partial pressure. For instance, concerning the water vapor permeability of hydrophilic polymer films, the water solubility and diffusion coefficients increase when the water vapor differential partial pressure increases because of the moisture affinity of the film (nonlinear sorption isotherm) and increased plasticization of the film due to water absorption<sup>39, 111</sup>. The film thickness can also influence permeability when using film-forming materials that do not behave ideally.

Hence, it should be noted that the permeability of edible films is a property of the film-permeant complex under defined ambient conditions (temperature and humidity).

Using sorption curves, it is quite easy to determine the effect of temperature and relative humidity on solubility of the permeant in the material. In contrast, it is more difficult to determine the nature of the functional relationship between diffusivity and temperature or water content<sup>111</sup>. Various theories, including the free volume theory, have been put forth to explain this functional relationship<sup>82</sup>. According to the free volume theory<sup>22, 123</sup>, molecular diffusion results from redistribution of the free volume in the material. This diffusion is only valid if the size of the free volume faults is greater than the critical value defined by the size of the diffused molecule. This value can be reached after a temperature increase. At  $T < T_g$ : mobility is controlled by the preexistence of pores in the glassy material, at  $T > T_g$ : polymer relaxation and porosity influence mobility<sup>25</sup>. The free volume theory allows one to qualitatively predict variations of  $D$  relative to the difference between the temperature and the glass transition temperature ( $T_g$ ). This theory is especially valid in the  $T_g$  to  $T_g + 100^\circ\text{C}$  range.

There is usually a difference between water vapor and gas permeability ( $\text{CO}_2$ ,  $\text{O}_2$ ) of the same film. According to Banker<sup>8</sup> and Kester & Fennema<sup>73</sup>, gas diffusion is crucial for gas permeability, whereas both sorption and diffusion are essential for moisture transfer.

Gravimetric methods are generally used to measure water vapor permeability<sup>1, 7</sup>. According to these techniques, the film is attached to a cell containing a desiccant and the differential partial pressure of the water vapor is kept constant by placing the cell in an extremely humid atmosphere. The opposite configuration is also possible but may lead to differences in the results, as is the case with chocolate films<sup>13</sup>. The time course of the weight gain of the cell allows calculation of the water vapor transmission coefficient (WVTC in  $\text{g}/\text{m}^2\cdot\text{day}$ ) and the "apparent" water vapor permeability constant ( $P_{\text{app}}$  in  $\text{g}\cdot\text{mm}/\text{m}^2\cdot\text{day}\cdot\text{mmHg}$ ).

The moisture barrier properties can also be monitored directly via variations in the water content (or water activity) of the different components. When this technique becomes too complex or difficult to carry out or interpret, food system models can be used<sup>13, 60</sup>.

Gas permeability (air oxygen, carbon dioxide, nitrogen, etc.) can be measured with air porosity meters or specialized cells for specific measurements <sup>3, 90</sup>.

The sorption isotherms of water and gas must be measured in order to calculate their solubilities in the material and evaluate the effect of humidity on film performance.

### **b- Gas barrier properties**

Materials with suitable oxygen barrier properties are required to protect oxidizable foods (to reduce rancidity and vitamin loss), but some permeability to oxygen, and especially to CO<sub>2</sub>, is essential for fresh fruit and vegetable coatings. Some biopolymer-based packaging has impressive gas barrier properties, especially against oxygen. The oxygen permeabilities of various edible and non-edible films are given in Table 1.

Hydrocolloid films have good oxygen barrier properties when they are not moist. Gelatin films can be used to protect frozen meats from rancidity <sup>74</sup>, to coat candies and dried products <sup>46</sup> and to microencapsulate flavors <sup>4</sup>. When moisture is present, the macromolecule chains become more mobile which leads to a substantial increase in oxygen permeability <sup>80</sup>.

Lipids, which are very often used to delay water transfer as described later, also have significant oxygen barrier properties.

According to Blank <sup>15, 16</sup>, lipids made up of linear saturated fatty acids, fatty alcohols and fatty acid esters containing 16 or more carbon atoms have the best oxygen barrier characteristics. An increase in the degree of unsaturation or branching and reduction in the length of the carbon chain lowers oxygen permeability. The following barrier efficiency order was observed by Kester & Fennema <sup>71</sup>: stearic alcohol > tristearine > beeswax > acetylated monoglycerides > stearic acid > alkanes. These differences can be explained by the presence of pores or cracks, the lipid content, homogeneity of the composition, density of the network, which is dependent on the polymorphic shape and orientation of the chains and morphological differences in the lipid layers (as viewed by electron microscopy) <sup>71, 73</sup>.

The development of edible films and coatings with selective gas permeability could be very promising for controlling respiratory exchange and improving the conservation of fresh fruits and vegetables. Composite films of carboxymethyl cellulose and fatty acid sucroesters appear to have suitable oxygen barrier properties while remaining relatively permeable to CO<sub>2</sub> <sup>30, 87</sup>. This type of film was applied to refrigerated bananas and caused a 5-fold reduction in oxygen transfer, whereas CO<sub>2</sub> exchange was only reduced by about half <sup>10, 11</sup>. However, this effect is dependent on the type and variety of fruit and temperature <sup>12, 116</sup>.

The selectivity coefficient of a film relative to two gases is defined as the ratio of the respective permeabilities of these gases under the experimental conditions. This selectivity is the basis for gas permeation procedures. Concerning oxygen and carbon dioxide, the relative solubility of CO<sub>2</sub> in water explains its high permeability in hydrophilic materials <sup>111</sup>. The

selectivity coefficient relative to these two gases is therefore dependent on the moisture content of the film <sup>111</sup>.

### c- Lipid and solute barrier properties

Oil penetration into foods to be fried (breaded fish or meats) or dried by frying (e.g. potato chips or fruits such as bananas) can be reduced by precoating these foods with lipid-resistant hydrophilic materials <sup>27</sup>.

Moreover, solute penetration during freezing of meats and seafoods in brine, or during osmotic dehydration of fruit and vegetable pieces, which is a considerable limitation in these processes, can be reduced by prior application of films that are resistant to the solutes in question <sup>50</sup>.

Certain specific additives (antimicrobial agents, antioxidants, nutritional additives, flavors, coloring, etc.) can be incorporated in edible films to obtain localized functional effects (usually on the surface of the food) at very low mean additive concentrations. Torres et al. <sup>120</sup> used a film composed of zein, aceto-monoglycerides and glycerol to maintain a high surface concentration of sorbic acid on an intermediate moisture cheese analog. The coating very significantly slowed migration of the sorbic acid. Diffusion of sorbic acid in this film was at  $3\text{--}7 \cdot 10^{-11} \text{ m}^2\cdot\text{s}^{-1}$ , which represented a 150- to 300-fold lower level than that in the food mass. The increased microbiological stability on the surface of this intermediate moisture cheese was confirmed by counts after surface-seeding of *Staphylococcus aureus* <sup>119</sup>. Motycka and Nairn <sup>94</sup> and Vojdani and Torres <sup>126</sup> studied the diffusion of benzoic acid and sorbic acid salts in lipid coatings (stearic alcohol, stearic acid and waxes) and composite films (cellulose derivatives and fatty acids). These materials significantly decreased the permeability to benzoic acid and sorbic acid. They could thus be recommended for maintaining high surface concentrations of antimicrobial agents.

Guilbert <sup>49</sup> developed a coating composed of a casein film containing sorbic acid and treated with a cross-linking agent. When this film was used to coat a food product with a moisture activity ( $A_w$ ) of 0.95, there was more than 30% surface retention of sorbic acid after 35 days storage. When the same protein film was used to coat dried fruits, with  $A_w$  0.85, the shelf life was increased from only a few days to over 40 days after contamination with osmophilic yeasts and moulds. Guilbert <sup>49</sup> also measured the retention of a tocopherol in gelatin films used on the surface of margarine. After 50 days storage, no migration was observed when the film was pretreated with a cross-linking agent (tannic acid), whereas without a film, a tocopherol diffusion was as found to be as high as  $10\text{--}30 \cdot 10^{-11} \text{ m}^2\cdot\text{s}^{-1}$ .

### d- Moisture barrier properties

Films with suitable moisture barrier properties are required for a great number of applications. Indeed, control of the moisture content and activity of heterogeneous food components or of the elements of a mixture influences the microbiological, physico-chemical and organoleptic characteristics of the food.

Surface drying of certain fresh or frozen foods or, conversely, moisture regain of dry or intermediate moisture foods, can be reduced by using films that are good barriers to moisture migration.

In order to conserve the different crunchy and soft textures, it is essential to reduce moisture exchange between compartments of heterogeneous foods (e.g. pizza, quiche, cakes or biscuits) or between the components of mixtures (e.g. aperitif mixes, breakfast mixes with dried fruit and/or cereals) with different water activity levels. In many cases, the only realistic technique to halt moisture exchange involves using edible barrier layers at the interfaces and between compartments or elements of mixtures<sup>50, 67, 68, 69</sup>.

Vegetal and microbial gums, starches, soluble cellulose derivatives and many proteins are used to form films which often have poor moisture barrier properties especially at high relative humidity. The use of such films as protective layers against moisture exchange (although described in many studies and patents) is limited to providing short-term protection for dried foods such as dried fruit<sup>35, 117</sup>.

Sugar coatings applied by centrifugal turbine action have interesting moisture barrier properties. Most hydrophilic groups of the sucrose molecule are thus involved in intermolecular linkage of the tridimensional crystal arrangement. Breakage of this structure can only occur above a certain energy level, i.e. above a certain water activity level at a given temperature (about 0.80 at 25°C)<sup>19</sup>. At lower  $A_w$  levels, water diffusion and especially the water solubility coefficient are very weak.

Moreover, according to its sorption isotherm<sup>13</sup>, the moisture content of chocolate is very low within the intermediate moisture range. This explains the suitable moisture barrier properties of chocolate, which have long been used even to coat liquids (e.g. liqueur chocolates).

Many lipid compounds, such as animal and vegetable fats, aceto-glycerides, surfactants and waxes<sup>2, 33, 34, 81, 85</sup>, have been used in the formation of edible films and coatings because of their excellent moisture barrier properties (Table 2).

Waxy coatings on fresh fruit and vegetables thus reduce weight loss due to dehydration during storage by 40-75%<sup>18, 31, 53, 61, 104</sup>.

Some edible lipid or derivative films with good moisture barrier characteristics have been patented<sup>26, 27, 121, 122, 127, 129</sup>.

Due to the weak polarity of lipid compounds and their ability to form dense organized molecular networks after cooling, the water remains relatively immobile and insoluble (quite straight sorption isotherm up to high relative humidities). The moisture barrier capacities of different films can be classified in decreasing order of efficiency, as follows: waxes > lipids



and solid fatty acids > lecithin, aceto-glycerides > liquid oils. This efficiency order was confirmed by Kester & Fennema<sup>72</sup> in a study on the resistance of various lipids, heated and absorbed into filter papers, to water vapor transmission.

The composition, fusion, solidification range and crystalline structure (polymorphic shape) of lipids and derivatives, in addition to the interactions with water, oxygen and other components of the food product, influence the physico-chemical, functional and organoleptic properties of lipid films<sup>71, 73</sup>.

Moisture permeability rises substantially when the proportion of liquid lipids increases. Solidification of lipids (especially saturated) in a densely organized crystalline structure results in a very significant reduction in moisture permeability<sup>58, 70, 81, 128</sup>.

Some surfactants, when applied as a thin surface layer, effectively inhibit water evaporation. They reduce water activity on the surface (surface  $A_w$ ) of the food product, thus substantially slowing the rate of water evaporation. This effect depends on the structure of the surfactant/water system, i.e. on the temperature, surfactant content, length of the carbon chain and degree of saturation. Saturated fatty alcohols with 16-18 carbons and the corresponding monoglycerides (glycerol monopalmitate and monostearate) are the most effective, with fatty acids and unsaturated monoglycerides being less effective<sup>109</sup>.

Lipids and derivatives can form good barriers to moisture transmission, but these compounds have certain drawbacks with respect to application, mechanical and chemical stability and/or organoleptic quality. Hence, lipid-hydrocolloid associations have been investigated often<sup>20, 27, 37, 40, 41, 43, 44, 48, 58, 59, 60, 67, 68, 69, 86, 110</sup>, and patented<sup>23, 24, 51, 54, 112, 114, 124</sup>. These films, which can constitute a better water vapor barrier than synthetic material such as low density polyethylene (Table 2), can be applied as emulsions, suspensions and dispersions of non-miscible compounds, or in successive layers (films and multilayer coatings) or in a solvent solution. The coating operation affects the barrier properties of the film. According to Schultz et al.<sup>110</sup> and Gontard et al.<sup>40, 41</sup>, who investigated the moisture permeability of films composed of demethoxylated pectins or gluten and various lipids (waxes, fatty acids, etc.), it is better to form two successive layers than to apply a dispersion in solvent. Kamper and Fennema<sup>58, 59</sup> carried out detailed studies of films composed of soluble esters, cellulose and a mixture of palmitic and stearic acids and demonstrated that application of solvent solutions (ethanol/water) resulted in reducing moisture permeability by 10-fold relative to bilayer systems. Variations in homogeneity and/or structure (size, form and orientation of the crystals) of the lipid layer affect film permeability and could be related to the coating operation.

Guilbert<sup>48</sup> developed a multicomponent film composed of gelatin or casein and carnauba wax and glycerol monopalmitate and monostearate. This film, which was applied as an emulsion and then acidified with lactic acid after drying, showed good water vapor barrier properties. Composite films of casein and aceto-glycerides or wax applied as an emulsion

were also investigated by Krochta et al.<sup>78</sup> They showed that lowering the pH of the film to the isoelectric point of casein reduced water vapor transmission by half.

A composite film (a mixture of hydroxypropylmethylcellulose and fatty acids) developed by Kamper & Fennema<sup>59</sup> was tested as a moisture barrier between two compartments of a heterogeneous food product (pizza-type foods), and the results indicated an increase from 20 days to more than 70 days in the shelf life of the frozen product without any loss in crust crispiness<sup>60</sup>. The water vapor barrier properties of this film were excellent up to 90% relative humidity, above this level hydration caused structural loss. To improve the moisture barrier properties at high humidities, Kester & Fennema<sup>67, 68</sup> coated this film with a thin layer of beeswax. The water vapor permeability of this film was close to that of polyvinyl chloride and low density polyethylene films (Table 2), and it remained constant at all relative humidity levels (up to 97%). Kester & Fennema<sup>68</sup> were able to correlate permeability with the morphology of the lipid components by electron microscopic analysis. The film was translucent, had suitable mechanical properties, and was an effective barrier to water transmission when tested with pizza-type frozen foods<sup>69</sup>. The film was not discernable when the food was eaten hot (melting point of the film: 80-85°C).

Using the falling film technique, Clark & Shirk<sup>21</sup> studied the semi-industrial application of a cellulose acetoglyceride and acetobutyrate coating (marketed under the "LEPAK" trademark by the American Cyanamid Co.) for surface protection of frozen fish and meats. They found that this film provided excellent protection (against discoloration, dehydration, microbial development, etc.), which was close to that obtained with non-edible films.

## CONCLUSION

This research provides evidence of the multiple advantages of using edible and biodegradable packaging made from biopolymers. Investigations on this type of packaging call on the use of biochemistry, food science and synthetic polymer technology techniques. The studies presented here have demonstrated a number of characteristics of food macromolecules that make them suitable for the formation of different types of wrappings and films. The use of these properties and their ability to be modified and controlled thus opens a new field of application for these macromolecules in a non-food sector, for the manufacture of biodegradable packaging. Problems resulting from the disposal of synthetic polymer packaging have caused a boom in research to obtain biodegradable products from biological macromolecules. This biodegradable objective has been partially reached by the addition of synthetic agricultural macromolecules (starch, proteins, etc.). Research and development is required to develop packaging material composed entirely of renewable biodegradable

macromolecules from agricultural products that have good performance characteristics and are economical. This is essential for purposes of environmental protection and to create a new outlet for agricultural products.

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## Legends

**Figure 1:** Different approaches to make "bio-packaging" from agricultural raw materials

**Figure 2:** Effect of pH and ethanol concentration of the film-forming solution on wheat gluten film opacity <sup>38</sup>.

**Figure 3:** Effect of gluten concentration and pH of the film-forming solution on wheat gluten film puncture strength <sup>38</sup>.

**Figure 4:** Effect of pH and ethanol concentration of the film-forming solution of wheat gluten film solubility and disintegration in water after 24 h immersion and agitation <sup>38</sup>.

# Raw material

origin

renewable

non-renewable

**agricultural**

**petrochemical**

basic material

substrate

polyolefines...

microorganisms

edible  
packaging

thermoplastic  
starch

polyesters

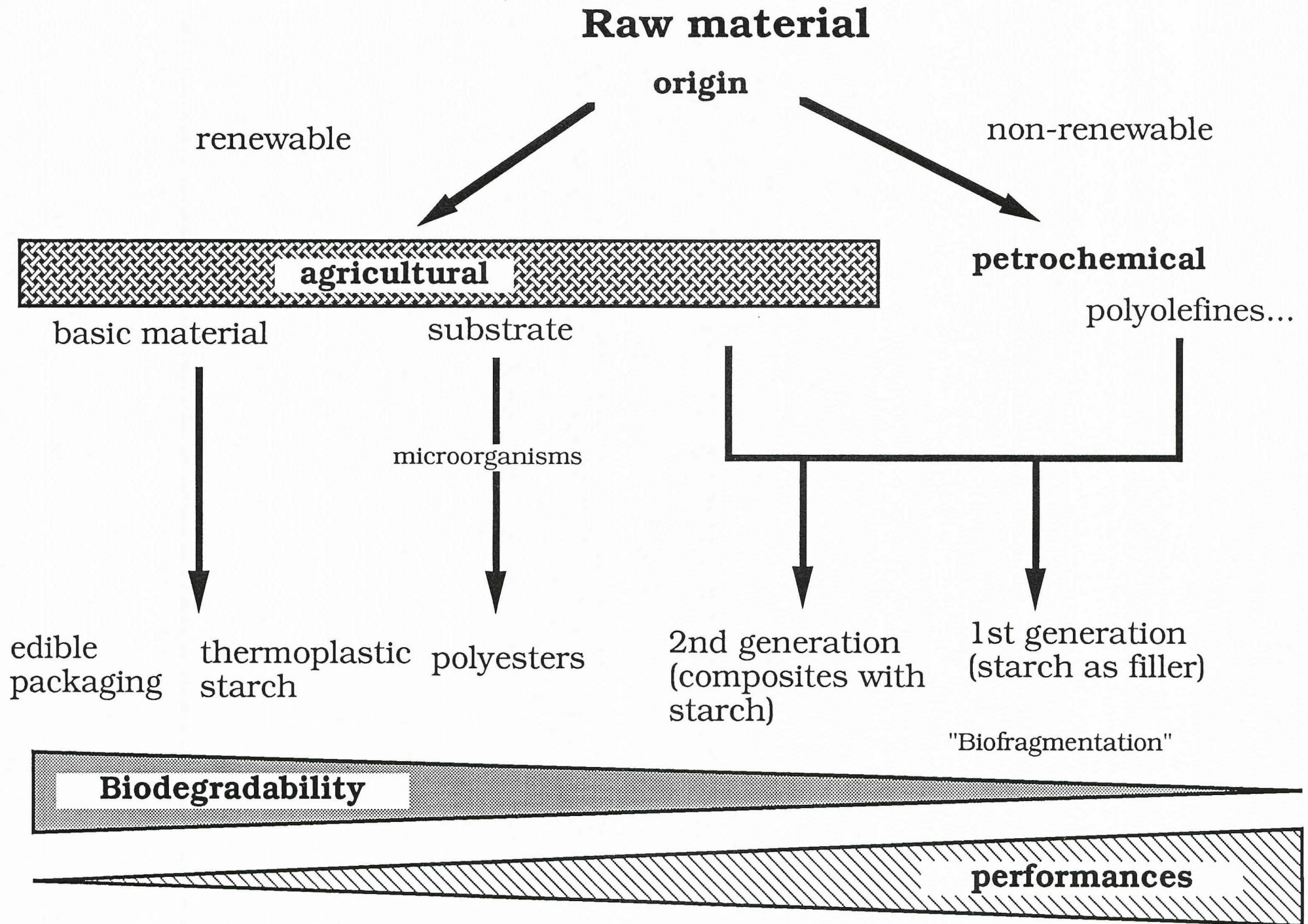
2nd generation  
(composites with  
starch)

1st generation  
(starch as filler)

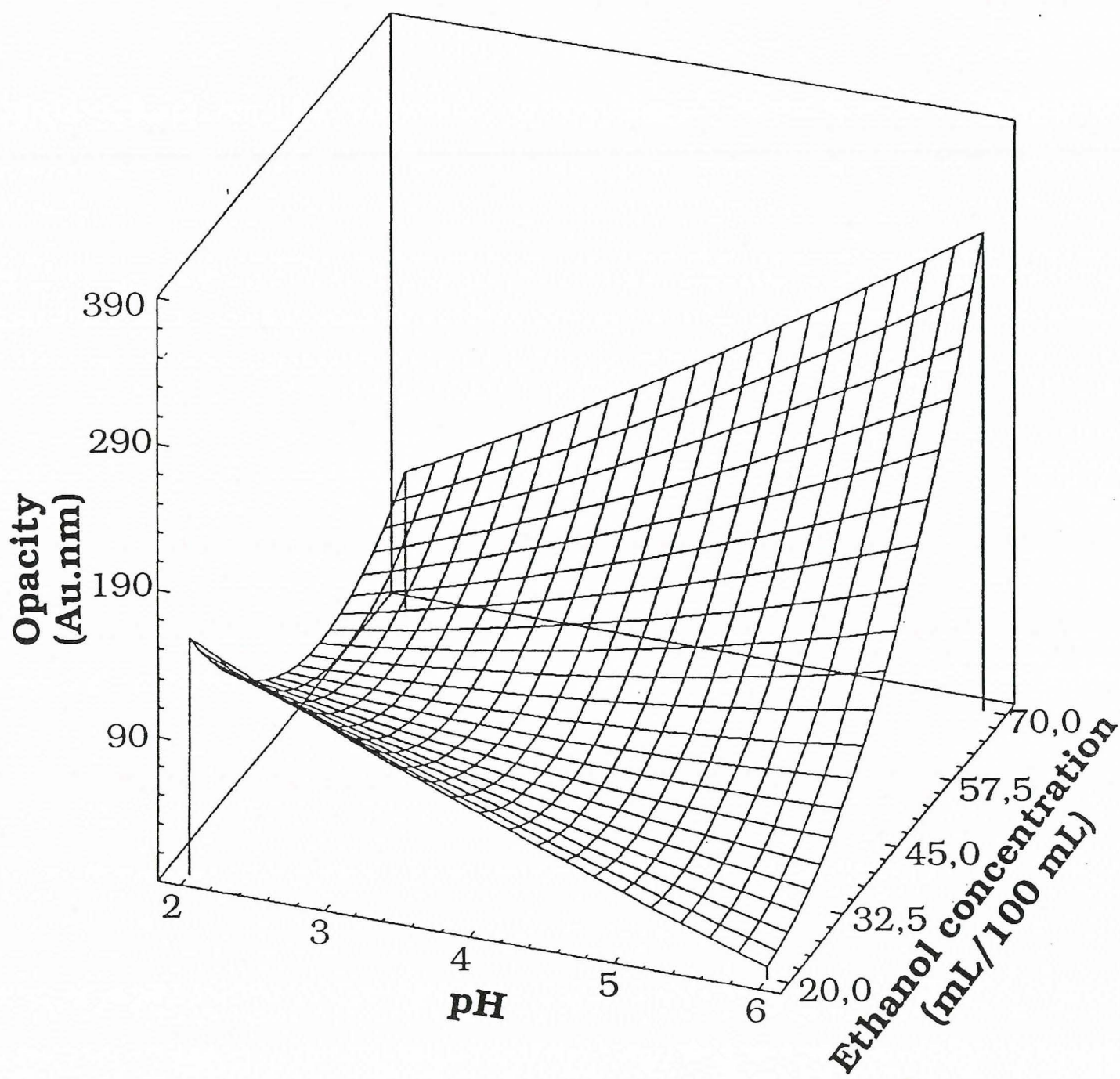
"Biofragmentation"

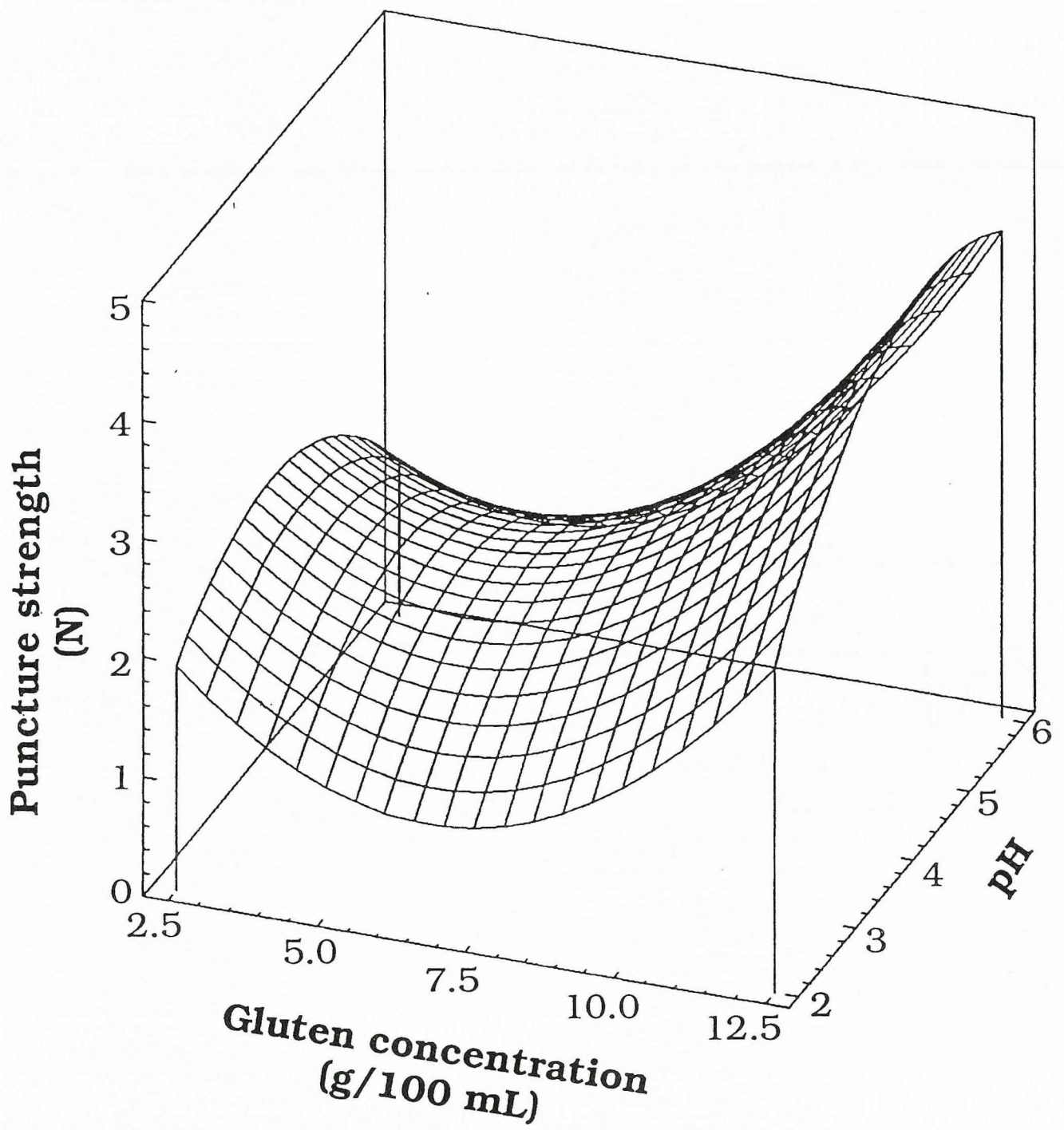
**Biodegradability**

**performances**









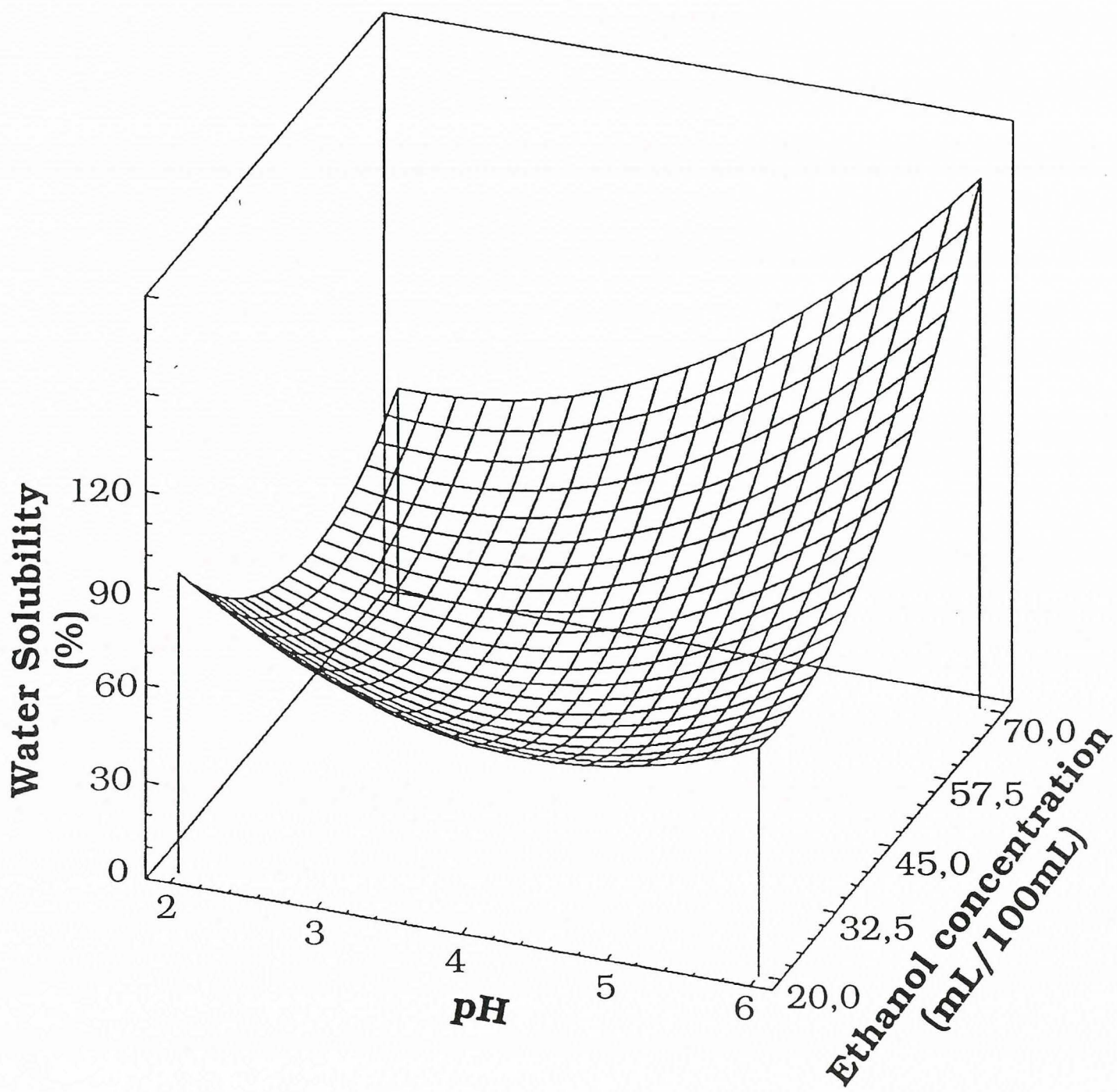




Table 1- Oxygen permeability of various films.

FILM	T(°C)	X (mm)	Oxygen permeability 10 <sup>12</sup> .g.cm./cm <sup>2</sup> .sec.mmHg.
Polyethylene (low density)	25	0.025	0.50
Starch	24	0.79	0.42
Polyethylene (high density)	25	0.025	0.125
Gliadins and glycerol	23	0.10	0.089
Acetostearin	26	0.17	0.030
Amylomaize	25	0.05	0.0325
MC/HPMC and beeswax	25	0.051	0.021
Gluten and glycerol	23	0.11	0.016
Beeswax and C <sub>18</sub> -C <sub>16</sub> MC/HPMC	25	0.045	0.007
Waxed paper	25	-	0.005-0.075
Cellophane	25	-	0.001

according to references: 3, 37, 43, 44, 63, 64, 85, 90.

x is film thickness, T is temperature.

HPMC is hydroxypropylmethyl cellulose, C<sub>18</sub> and C<sub>16</sub> are stearic and palmitic acids, MC is methyl cellulose.

- data not available in literature cited.

**Table 2 - Water vapor permeability of various films.**

FILM	T (°C)	$\Delta p$ (mmHg)	x (mm)	Permeability (g.mm/m <sup>2</sup> .mmHg.day)
Starch, cellulose acetate	37.7	49.2-15.7	1.19	29.3
Sweet milk chocolate	26.7	26.3-0	1.91	9.94
Pectin	25	19.2-7.3	0.036	8.2
Casein-Gelatin treated with lactic acid	30	28.9-18.5	0.25	7.1
hydrogenated soya and cotton oils, HPMC	25	20.0-0	0.12	1.74
Gliadins and Glycerol	30	32.2-0	0.05	1.36
Acetylated glycerol monostearate	21.1	18.8-14.1	1.75	1.215
Gluten and Glycerol	30	32.2-0	0.05	1.05
Gluten, DATEM and Glycérol	30	32.2-0	0.05	0.55
Glutenins and Glycérol	30	32.2-0	0.05	0.75
Zeine and oleic acid	37.8	44.7-0	0.04	0.30
Tempered cocoa butter	26.7	26.3-0	1.61	0.288
Palmitic and stearic acid on HPMC	25	23-15.4	0.04	0.253
Dark chocolate	20	14.1-0	0.61	0.14
Cellulose acetate	37.7	44.3-0	0.025	0.113
C18-C16 MC/HPMC	25	20.0-0	0.02	0.035
Gluten and Monoglyceride	30	32.2-0	0.11	0.024
Polyethylene (low density)	37.7	44.3-0	0.025	0.010
C18-C16 MC/PEG and beeswax	25	20.2-0	0.056	0.0075
C18-C16 MC/HPMC and beeswax	25	20.2-0	0.051	0.0075
C18-C16 HPMC/PEG	25	20.2-0	0.04	0.0050
Gluten and beeswax	30	32.2-0	0.09	0.0048
Beeswax	25	20.0-0	0.12	0.0025
Waxed paper	37.8	46.7-0	-	0.0016-0.125
Paraffin wax	25	20.0-0	0.66	0.0002
Aluminium foil	37.7	44.3-0	0.025	0.00006

according to references: 3, 13, 37, 38, 39, 43, 44, 48, 50, 58, 59, 64, 68, 69, 81, 85,

x is film thickness, T is temperature,  $\Delta p$  is water vapor pressure gradient.

DATEM is Diacetyl Tartaric Ester of Monoglyceride, HPMC is hydroxypropylmethyl cellulose, C18 and C16 are stearic and palmitic acids, PEG is polyethylene glycol, MC is methyl cellulose.

- data not available in literature cited.