LIPIDS AND BIOPACKAGING. USAGE OF LIPIDS IN EDIBLE FILMS

Mirjana Milovanović and Ksenija Pičurić-Jovanović

Abstract: Packaging is very important for providing the food quality as its barrier to water vapor, aroma, and migration between the food and the environment. Different kinds of biopackaging of lipids are presented. It is especially pointed to the lipids used in edible films, mainly for their efficiency as water-vapor barriers. The structure, degree of saturation, chainlength and distribution of lipids in film are discussed. The performance of edible films with lipids is also lower than some commercially used synthetic films e.g. barriers and mechanical properties, but their main advantage is to be easily and rapidly degradable.

Key words: Lipids, edible film, biopackaging.

Introduction

In the last 20 years, petrochemical polymers, called plastics, have been used for packaging. These polymers have high performance and low cost but cause a lot of problems when used for food packaging e.g. environmental pollution, a low solution in comparison with biodegradable biopolymers. Transfer of substances from the plastics (e.g. additives, monomers, plasticizers, solvent residues, etc.) to the foods can occur. However, the composition of packed foods (e.g. fat content, flavorings, pH, etc.) may influence the characteristics of plastics (Manheim, 1990). Especially fat, migrating into plastics like polyethylene or polypropylene,
increases the mobility of plastic film ingredients. It can also increase the migration of plastic molecules into the food and change the properties of packaging material. This migration tends to increase with fat content and also is due to the higher solubility of the migrating organic compounds in fat, compared to water (Kočh, et al, 1978; Goydan, et al, 1990). From these observations then arises both the need to find biodegradable packaging polymers to solve the problem of pollution and the need to make edible polymers with food-grade additives to prevent unwanted migrations.

Applications of edible films are numerous and different because they provide the protection for moisture and oxygen between the food and the environment parts in the heterogeneous food. They also improve mechanical handling and enhance the food appearance. Edible films can be used as carriers of fungicides, antioxidants, antibacterial agents, coloring agents, flavorings, vitamins and growth regulators. The aim of this review is to focus on the importance of lipids in biopackaging and in edible films in particular.

**Biodegradable films**

There are three kinds of biodegradable films. The first one are some *synthetic polymer/biopolymer mixtures* films which exist in native starch (5-20%) and prooxidative and autooxidative additives with synthetic polymers (Krupp, et al, 1992). Their biodegradability is highly controversial and is limited to the fragmentation into small particles. The second type, *microbial polymers* are produced by fragmentation of natural substances whose films are made from polyhydroxybutyrate and polylactic or polyglycolic acids obtained from some biotechnologies. They are totally degradable, but their applications are currently limited by high price. The last one are *agricultural polymers*, which are used as packaging material and are made from polymers of agricultural origin (e.g. grains, proteins, starches). Thermoplastic applications of starches are limited by their sensibility to water. Relatively insoluble films can be obtained by crosslinking cotton proteins in a film solution (Marque, et al, 1995). Moreover, they are economical because of low cost of raw materials and are promising in creating new markets for agricultural products.

Biopackaging of lipids in edible films are important because of their hydrophobic character, they are moisture transfer barriers and microbiological degradation can also preventing by them.

**Lipid-water interactions**

The interactions of lipids from edible films with other constituents of films and food, such as water proteins and sugars need a considerable attention. Lipid
molecules in water have several structures as shown in Figure 1. They make forms of the micelles, shown as monolayers or bilayers, because the water has such a strong cohesive self-attraction that it repels a valuable hydrophobic effect (Israelachivili, 1991). Variation of the polarity of lipids can explain different efficiencies of lipids as water-vapor barriers in edible films. According to their polarity, biologically active lipids are classified (Small, 1986) and listed in Table 1.

![Micelle](image1.png) ![Inverted Micelle](image2.png) ![Bilayer](image3.png) ![Bilayer Vesicle](image4.png)

Fig. 1. - Lipids structures formed in the presence of water

<table>
<thead>
<tr>
<th>Class</th>
<th>Surface properties</th>
<th>Bulk properties</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nonpolar</td>
<td>Not spread to form monolayer</td>
<td>Insoluble</td>
<td>Paraffin oil; waxes</td>
</tr>
<tr>
<td>Polar:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Class I: Insoluble, nonswelling amphiphiles</td>
<td>Spread to form stable monolayer</td>
<td>Insoluble or very low solubility</td>
<td>Tri-, diglycerides; cholesterol, vitamins A, D, E, K</td>
</tr>
<tr>
<td>Class II: Insoluble, nonswelling amphiphiles</td>
<td>Spread to form stable monolayer</td>
<td>Insoluble but swell in water to form liquid crystals</td>
<td>Phospholipids, monoglycerides</td>
</tr>
</tbody>
</table>

Tab. 1. – Classification of biologically active lipids
Waxes belong to nonpolar lipid class. They have no polar constituents (hydrocarbons), nor do they possess a hydrophilic part in the molecule, so they can not interact with water. This explains why waxes are the most efficient lipid barriers to water-vapor transfer in edible films. They are also used in emulsion for coating fruits and vegetables (Kester, 1986). Triglycerides belong to the polar lipids, class I. They are insoluble in the bulk water, but will spread at the interface to form a stable monolayer (triacetin and triburyrin). Fatty acids as well as fatty alcohols with long chains (palmitic acid, stearic acid, lauric acid and stearyl alcohol) belong to the same class. Monoglycerides belong to class II, depending on their chainlength. Concerning class II, lipids are insoluble in water, but water is soluble in the hydrophilic part of their structure, causing them to swell. In the absence of water, they are sparingly soluble in typical organic solvents. Thus, they are good emulsifiers. Interesting structures result from the interaction of water with monoglycerides. In a low water concentration they make inverted micelles with the polar heads toward the inside, and at higher water concentrations micelles are of the normal type with the polar groups protruding into the aqueous phase (Figure 1).

Monoglycerides are used in edible films as good emulsifiers, especially for stabilising emulsified film but also for increasing adhesion between the two parts with different hydrophobicity, e.g. between the film and the food or between the lipidic layer and the hydrocolloid layer in the bilayer film (Debeaufort, and Volye, 1995). The properties of lipids and their interactions with proteins and polysaccharides are described and can be also extrapolated to better understand and improve biopackaging performances. A review concerning the influence of lipids is presented herein, especially their use in edible films.

**Lipids in edible films**

A packing film must, in general, be resistant to breakage and abrasion (to protect the food and provide easy handling) and flexible (enough plastic to adapt to possible deformation of the filling without breaking). Furthermore, it must be a barrier against water-vapor and oxygen transfer, which are the main factors responsible for organoleptic degradation, physicochemical modification and microbiological spoilage of the food during preservation.

In general, permeability for water and oxygen decreases as the chainlength of lipid increases (Mughrabi, and Krockta, 1994). In Tables 2 and 3 some values of water-vapor permeabilities in some edible and plastic films are reported. The lipids most used are fatty acids with the number of carbon atoms between 14 and 18, fatty alcohols as well as stearyl alcohol, hydrogenated and nohydrogenated vegetables oils, and waxes (paraffin, candelilla). When the hydrocarbon chainlength was increased up to 16-18 carbons for fatty alcohols, moisture-barrier was improved. For fatty acids, barrier properties were augmented with an increase of chainlength from 12 to 18 carbon atoms, but from 18 to 22,
barrier properties decreased. This behaviour could be explained by the morphological arrangement of fatty acid chains with respect to the polymers effects the barrier properties of the film. Chitosan-lipid-based display better efficiency against moisture transfer when the lipid is incorporated in the matrix, such as the film with lauric acid (Wong, et al, 1992).

Tab. 2. – Water-vapor permeability of lipid-based

<table>
<thead>
<tr>
<th>Film</th>
<th>T (°C)</th>
<th>ΔHR (%)</th>
<th>I (μm)</th>
<th>Permeability ((10^{-11} \text{ g m}^{-1} \text{s}^{-1} \text{Pa}^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Myristic acid ((C_{14:0}))</td>
<td>23</td>
<td>12-56</td>
<td>50</td>
<td>3.47</td>
</tr>
<tr>
<td>Palmitic acid ((C_{16:0}))</td>
<td>23</td>
<td>12-56</td>
<td>50</td>
<td>0.65</td>
</tr>
<tr>
<td>Stearic acid ((C_{18:0}))</td>
<td>23</td>
<td>12-56</td>
<td>50</td>
<td>0.11-0.22</td>
</tr>
<tr>
<td>Paraffin wax</td>
<td>23</td>
<td>0-85</td>
<td>150</td>
<td>0.03-0.06</td>
</tr>
<tr>
<td>Candelilla wax</td>
<td>25</td>
<td>0-100</td>
<td>100</td>
<td>0.018</td>
</tr>
<tr>
<td>Peanut oil</td>
<td>25</td>
<td>22-44</td>
<td>230</td>
<td>13.8</td>
</tr>
<tr>
<td>Hydrogenated cotton oil</td>
<td>27</td>
<td>0-100</td>
<td>1560</td>
<td>0.13</td>
</tr>
<tr>
<td>Cocoa butter</td>
<td>25</td>
<td>22-44</td>
<td>60</td>
<td>3.6</td>
</tr>
</tbody>
</table>

T (°C), temperature during transfer  
ΔHR, relative humidity gradient  
I, thickness

Tab. 3. – Water-vapor permeability of composite and synthetic films

<table>
<thead>
<tr>
<th>Film</th>
<th>T (°C)</th>
<th>ΔHR (%)</th>
<th>I (μm)</th>
<th>Permeability ((10^{-11} \text{ g m}^{-1} \text{s}^{-1} \text{Pa}^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bilayers systems</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MC + paraffin wax</td>
<td>25</td>
<td>22-84</td>
<td>87</td>
<td>0.2-0.4</td>
</tr>
<tr>
<td>MC + beeswax</td>
<td>25</td>
<td>0-100</td>
<td>100</td>
<td>0.058</td>
</tr>
<tr>
<td>MC + carnauba wax</td>
<td>25</td>
<td>0-100</td>
<td>100</td>
<td>0.033</td>
</tr>
<tr>
<td>MC + candelilla wax</td>
<td>25</td>
<td>0-100</td>
<td>100</td>
<td>0.018</td>
</tr>
<tr>
<td>HPMC + stearic acid</td>
<td>27</td>
<td>0-97</td>
<td>19</td>
<td>0.12</td>
</tr>
<tr>
<td>Emulsified systems</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MC+PEG+myristic acid</td>
<td>223</td>
<td>12-56</td>
<td>50</td>
<td>3.5</td>
</tr>
<tr>
<td>HPMC+PEG+AM</td>
<td>21</td>
<td>0-85</td>
<td>150</td>
<td>8.2</td>
</tr>
<tr>
<td>Cellophane</td>
<td>25</td>
<td>22-84</td>
<td>20</td>
<td>5.6</td>
</tr>
<tr>
<td>Cellulose acetate</td>
<td>25</td>
<td>0-100</td>
<td>150</td>
<td>3.2</td>
</tr>
<tr>
<td>PVC</td>
<td>25</td>
<td>0-100</td>
<td>100</td>
<td>0.068</td>
</tr>
<tr>
<td>LDPE</td>
<td>38</td>
<td>0-90</td>
<td>25</td>
<td>0.07-0.097</td>
</tr>
<tr>
<td>HDPE</td>
<td>25</td>
<td>0-100</td>
<td>100</td>
<td>0.01</td>
</tr>
</tbody>
</table>

T (°C), temperature during transfer  
ΔHR, relative humidity gradient  
I, thickness  
MC, methylcellulose  
HPMC, hydroxypropylmethylcellulose  
PEG, polyethyleneglycol  
AM, acetylated monoglycerides  
PVC, polyvinylchloride  
LDPE, low density polyethylene  
HDPE, high density polyethylene
Additionally, some researchers have reported that the barrier properties increased with the degree of the saturation of the lipid. Films with paraffin and beeswaxes are more stable than those prepared with some polyunsaturated corn oil (Kamper and Fennema, 1984). They also observed a greater capacity to retard the transfer of water vapor in emulsion films. This could be explained by different nature of lipids used (stearic and palmitic acids) and by their different arrangement at the interface (emulsion) and surface (bilayer). Martin Polo showed that for paraffin and alkane based films, the greater the size or the number of crystals the more the permeability was reduced. The same authors also noted that the role of lipid phase depends on the morphology or type of the solid hydrophobic material (Martin Polo, 1992).

The mechanical properties of the films usually depend on the ability of film-forming substances to form strong or numerous molecular bonds between the chains. For the bilayer films, some lipids, such as fatty acids, monoglycerides, phospholipids, acetoglycerides are used to increase the flexibility of polymeric films. They can be considered plasticizers because they weaken the intermolecular forces between adjacent polymer chains. Unfortunately, this produced an increase in gas and water vapor permeability across the film (Caillegerin, et al, 1997).

Some factors, such as humidity and temperature, can influence the structure and physical state of lipids and, consequently their water-vapor barrier efficiency (Greener, and Fennema, 1992).

![Fig. 2. - Schematic view showing how lipid film was sealed to a cup with the aid of vinyl tape](image)

Figure 2 shows how the lipid film was sealed to the cup with the aid of vinyl tape. Beeswax was used because it is an excellent barrier to water vapor, is cheap, and because it can be legally added to some foods. Water is the most common plasticizer. At the relative high humidity, the polar groups of fatty acids and the
fatty alcohols in the wax, which stand between aliphatic chains under normal conditions, may be able to humidify the film sufficiently to influence its water vapor permeability. Permeability depends on diffusion and sorption of the penetrant. Water vapor permeance of the lipid films was calculated by the following equation:

\[ \text{Permeance} = \frac{J}{C_i - C_a} \]

Where: \( C_i \) is water vapor concentration inside the cup in g x m\(^{-3}\), \( C_a \) is water vapor concentration of the room in g x m\(^{-3}\), and \( J \) is water-vapor transmission through the film. \( J \) was determined by the gravimetric cup method (Karel, 1975). Generally, an increase of temperature causes an increase of diffusion; on the contrary, water sorption is favoured by a decrease in temperature.

Dried fruits too can be waxed or oiled to retard further loss moisture, which could result in surface crystallisation of sugar; such coatings also may inhibit the development of insect eggs or larvae under the fruit surface (Kochhar, and Rossel, 1982). Ethyl esters of fatty acids (C\(_{10}\)-C\(_{18}\)) have been used to coat grapes and plums, in the manufacture of waxy fruits (Sauréz, et al., 1984, and Pčurić-Jovanović, K., et al., 1993 and 1999).

Edible coatings with lipids are also currently used for frozen foods, such as meat and fish (Suchéll, et al., 1995). Coating of low-melting point acetylated monoglycerides, used alone or after applying a whey protein isolate solution, were effective in reducing the rate of moisture loss of frozen king salmon by 42-65% during the first 3 weeks of storage at -23°C. Another water-in-oil emulsion for frozen meat products has been patented; fats used included corn oil, cottonseed oil, soybean oil, and fats from some chicken, beef, or pork (Bauer, 1968).

**Conclusion**

In this work we discussed the importance of lipids in biopackaging, in particular in edible films. Lipids are used for their hydrophobic character as water vapor barriers. Their efficiency depends not only on chemical structure, degree of saturation, and physical state but also on their homogeneity in the film. A bilayer film is a better barrier than an emulsion film. Lipids, in general, have no influence on the mechanical properties of the films, but some of them (fatty acids, monoglycerides, phospholipids) are often used in the formulation of plasticisers. They increase flexibility by weakening intermolecular forces between polymer chains.

In general, edible films have lower barrier and mechanical properties than plastic films, but their main advantage is that they can be eaten and no waste is produced, they do not cause environmental pollutions and being biodegradable products. For this reason, more and more industries have recently become interested in the use of edible films.
REFERENCES


Received February 23, 2001
Accepted March 27, 2001
LIPIDI I BIOPAKOVANJE. PRIMENA LIPIDA U JESTIVIM FILMOVIMA

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Rezime

U ovom radu istaknut je značaj lipida kod biopakovanja sa posebnim osvrtom na jestive filmove. U ovoj oblasti lipidi su našli primenu u formiranju barijere isparljivosti, zbog svojih visokih hidrofobnih osobina. Njihova efikasnost zavisi ne samo od hemijske strukture, stepena zasićenosti i fizičkih karakteristika, već isto tako i od njihove homogenosti u filmu. Dvoslojni film formira bolju granicu isparljivosti od emulzionog filma. U osnovi lipidi ne utiču na mehaničke karakteristike filma, ali se neki od njih (masne kiseline, monogliceridi, fosfolipidi) često koriste kao plastifikatiri. Lipidi povećavaju fleksibilnost i plastičnost slabljenjem intermolekularnih sila između polimerizovanih lanaca. Jestivi filmove imaju slabije mehaničke i zaštitne granične osobine u odnosu na plastične-sintetičke filmove, ali je njihova osnovna prednost da su jestivi i ne zagaduju životnu sredinu, jer predstavljaju biodegradacione proizvode. Iz tih razloga u novije vreme, sve je veći interes za primenu jestivih filmove u prehrambenoj industriji.


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