Available online www.jsaer.com

***Journal of Scientific and Engineering Research*, 2017, 4(9):86-92**

Review Article

ISSN: 2394-2630
CODEN(USA): JSERBR

Lipid Based Edible Films

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Abstract Recently, food and packaging industries have been joining efforts to reduce the amount of food packaging materials. Edible food and coatings have become popular in the food industry, because they produce less waste, are cost effective, and offer protection after the package has been opened. The use of edible films in food products seems new, but food products were first covered by edible films and coatings many years ago. Chitosan films are examined under four headings. These are carbohydrate films, lipid films, protein films and complex films. Lipid compounds contain neutral lipids of glycerides. Lipids are commonly added to food coatings to impart hydrophobicity. Lipids are mainly used for their efficiently as a water-vapor barrier in edible films. The structure, degree of saturation, chain length, physical state, shape and dimension of crystal and distribution of lipids into the film influence the functional properties of the film. Wax and glycerides are examples of lipid based films.

Keywords Edible Films, lipid, wax, glycerides

Introduction

In the last almost half of a century, petrochemical polymers, which are called as plastics, have been being used for almost every field of food packaging. Although these polymers have a remarkable outcome in use as well as being charmingly cheap, they pose some problems regarding health and environmental pollution [1]. Regarding health problem, the polymeric materials are not inert. Therefore; chemical transfer of substances from plastic material to food can occur depending on the composition of food material [2]. Among composites fat has the strongest influence. As, it enhances the mobility of plastic film ingredients as well as increasing the migration of plastic molecules into food and altering the characteristics of packaging material [1]. This can be explained by that the solubility of migrating organic compounds in plastic material is better in fat comparing to water [3]. The other problem is about environmental policies, which we face in the fields of recycling and incineration. In order to overcome these two problems, edible polymers with food-grade additives and biodegradable packaging polymers should be promoted.

These polymers can be classified in 4 general groups. They are polysaccharides, proteins, lipids and complex, respectively. Among them polysaccharides and proteins have remarkable mechanical and optical properties, yet highly sensitive to moisture. Therefore they exhibit poor water vapour barrier properties. On the other hand, remaining these two groups, being lipids and polyesters, have a good water vapour barrier features [4].

There are three sort of biodegradable films present [4].The first one is synthetic polymer/biopolymer mixtures films which exist in native starch (5-20%) and prooxidative and autooxidative additives with synthetic polymers [1].Yet their biodegradability is highly controversial. The second one is microbial polymers which are produced by fermentation from agricultural substrates. Although they are completely recyclable and biodegradable, they can’t find a field to be used due to its high cost. The last type is agricultural polymers, which are used as packaging material and are made from polymers of agricultural origin such as: grains, proteins and starches. They are quite economical due to low cost of raw materials and are promising for creating new markets for agricultural products. Yet, there is one disadvantage. The more the level of biodegradability is, the less the barrier performance the product will exhibit [5].

The aim of this review is to emphasis on lipids in biopackaging and edible films. Lipids play a key role in forming a barrier to moisture which will result in preventing microbial and physicochemical deterioration. But the efficiency of lipid to be used depends on some factors like its structure, hydrophobicity, physical state and etc.

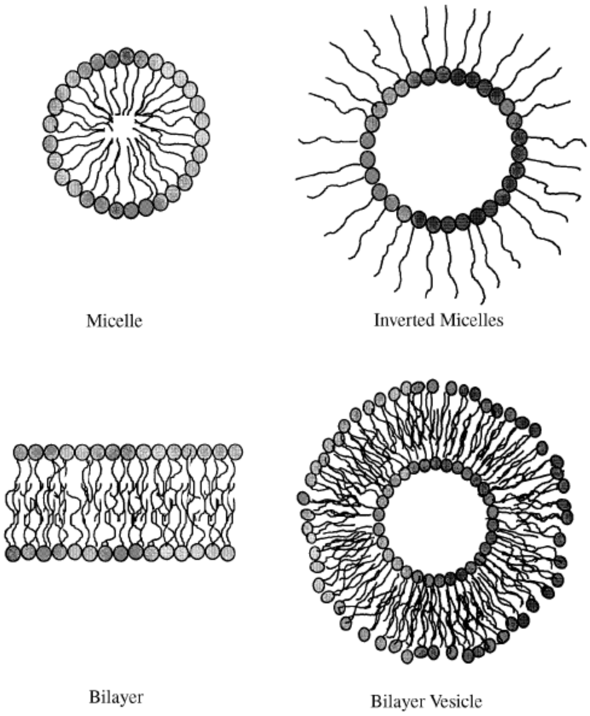

Figure 1: Lipids structures formed in the presence of water

Lipid-water interactions: The interaction of lipid with any constituents of food should be very well understood. Lipid molecules in water have 4 different structures shown in Figure 1. They make different kind of micelles since the water possesses such a strong cohesive self-attraction repelling hydrophobic effect [5].

Lipids used in biofilming are classified into 2 groups and 4 subgroups as shown in figure 2.

Roughly speaking lipids have 2 general groups which are polar and non-polar. Waxes belong to nonpolar lipid class. They don't posses any polar constituent like hydrocarbons, which is why they don't have an interaction with water. They are completely insoluble in the water. Moreover, they don't spread on the surface to form a monolayer [6]. That's why waxes are the most effective lipid barrier to water-vapor transfer in edible films. Most of papers/researches report a decrease in water vapor permeability owing to highly hydrophobic profile of lipid and among them waxes are the best to use [7]. Therefore they have been being used in different food products by many researchers.

Triglycerides, on the other hand, belong to class I of polar lipids. Although they are not soluble in bulk water, they will spread at the interface to form a stable monolayer. To be able to speak about their hydrophobicity, we have take a look at their structure first. Speaking roughly long-chain triglicerides are insoluble in water while short-chain triglicerides are partly soluble [5]. Adding palmitic, stearic, lauric acids and stearyl alcohol to edible films will enhance the moisture-barrier quality [6]. Kamper and Fennema stopped the transfer of water from tomato paste to crackers using a bilayer film made up of palmitic-stearic acid and hydroxypropylmethylcellulose in 1985 [8].

Monoglycerides belong to class II or III depending on their chain length. Regarding class II, lipids are not soluble in water whereas water is soluble in the hydrophilic part of their structure which lead them to swell. In the absence of water, they are sparingly soluble in typical organic solvent like hexane. Therefore; they exhibit good emulsifying properties. Interesting structures arise from the interaction of water with monoglycerides. In the presence of low water content they make inverted micelles with polar heads towards inside. In the presence of high water content, on the other hand, micelles exhibit a normal type with polar groups look toward aqueous phase as shown in figure 1 [5].

Monoglycerides are used in edible films as an emulsifier to stabilize emulsified film. Yet, last but not least use of monoglycerides is that they are used to enhance adhesion between two parts having different hydrophobicity. For instance, between the film and the food or between the lipidic layer and the hydrocolloid layer in the bilayer film [9].

Acetylated monoglycerides, which are emulsifiers in which acetic acid is bound with monoglyceride, are often used in edible film formulations to coat frozen food due to their plasticizer characteristics [10]

Classification of Biologically Active Lipids[a]

Class	Surface properties	Bulk properties	Examples
Nonpolar	Not spread to form monolayer	Insoluble	Paraffin oil; waxes with long-chain fatty acids
Polar			
Class I: insoluble, nonswelling amphiphiles	Spread to form stable monolayer	Insoluble or solubility very low	Tri-, diglycerides; cholesterol; vitamins A, D, E, K
Class II: insoluble, nonswelling amphiphiles	Spread to form stable monolayer	Insoluble but swell in water to form lyotropic liquid crystals	Phospholipids; monoglycerides
Class IIIA: soluble amphiphiles with lyotropic mesomorphism	Spread but form unstable monolayer owing to solubility in aqueous substrate	Soluble, form micelles above a critical micellar concentration; at low water concentrations, form liquid crystals	Detergents; lysolecithin; salts of long-chain fatty acids; gangliosides
Class IIIB: soluble amphiphiles, no lyotropic mesomorphism	Spread but form unstable monolayer due to solubility in aqueous substrate	Form micelles but not liquid crystals	Bile salts; rosin soaps; saponins

Knowing the features of only lipids regarding coating is not sufficient. To take a step forward, lipids' interactions with proteins and polysaccharides are needed to be well understood.

Lipids in Edible Films

It is expected from a packaging film to be resistant to breakage ad abrasion even in the worst circumstances. Furthermore, it should be plastic enough to adapt to possible deformation of the filling without breaking [4]. Since that organoleptic degradation mainly occur during storage due to oxygen and water vapor permeability's of the package, the packaging film must act as a barrier against oxygen and water vapor.

As mentioned above using lipids, protein or polysaccharides only by themselves is not sufficient. As, films made up of only one substance can either act as a good barrier or have a promising mechanical properties. Polysaccharides and proteins used for this purposes gives the material promising mechanical properties by establishing polymer interactions. Lipids, on the other hand, give the food material its good barrier properties, however, films including only lipids are generally too brittle. In tables 2 and 3 some values of water-vapor permeability's of some edible films as well as plastic films are shown.

The fatty acids mostly used for this purpose are waxes, nonhydrogeneted vegetable oils, fatty alcohols and fatty acids whose carbon atom number changes from 14 to 18.

Chitosan-lipid based films show better efficiency to moisture transfer when the lipid is uniformly incorporated in the matrix. It shows the importance of the morphological arrangement of the lipid within thechitosan matrix, as well [11].

Food applications of emulsion based edible films and coatings:

In this review, the food is divided into 4 groups: Fruits and vegetables, meat and meat products, dairy products and cereal products.

TABLE 2
Water-Vapor Permeability of Lipid-Based, Polysaccharide-Based, and Protein-Based Films

Film	T (°C)[a]	ΔHR (%)[b]	l (μm)[c]	Permeability (10^{-11} g·m^{-1}·s^{-1}·Pa^{-1})	Reference
Lipid-based					
Myristic acid ($C_{14:0}$)	23	12–56	50	3.47	35
Palmitic acid ($C_{16:0}$)	23	12–56	50	0.65	35
Stearic acid ($C_{18:0}$)	23	12–56	50	0.11–0.22	35
Paraffin wax	23	0–85	150	0.03–0.06	38
Candelilla wax	25	0–100	100	0.018	61
Peanut oil	25	22–44	230	13.8	62
Hydrogenated cotton oil	27	0–100	1560	0.13	63
Cocoa butter	25	22–44	60	3.6	62
Polysaccharide-based					
MC[d]	25	0–52	25	8.7–14.0	64,65
HPMC[e]	27	0–85	190	10.5	65
Protein-based					
Gluten + glycerol	25	0–100	/	4.4–13.2	66
Soja proteins	25	50–100	65	179–304	67
W-prot.[f] + PEG 400[g]	25	0–63	115	150	34
Na-cas[h]	25	0–100	50	15.5–32.7	34

[a]T (°C), temperature during transfer.
[b]ΔHR, relative humidity gradient.
[c]l, thickness.
[d]MC, methylcellulose.
[e]HPMC, hydroxypropylmethylcellulose.
[f]W-prot., whey proteins.
[g]PEG, polyethyleneglycol 400.
[h]Na-cas, sodium caseinate.

[5]

TABLE 3
Water-Vapor Permeability of Composite Films

Film	T (°C)[a]	ΔHR (%)[b]	l (μm)[c]	Permeability (10^{-11} g·m^{-1}·s^{-1}·Pa^{-1})	Reference
Bilayer systems					
MC[d] + paraffin wax	25	22–84	87	0.2–0.4	62
MC + beeswax	25	0–100	100	0.058	61
MC + carnauba wax	25	0–100	100	0.033	61
MC + candelilla wax	25	0–100	100	0.018	61
HPMC[e] + stearic acid	27	0–97	19	0.12	68
Emulsified systems					
MC + PEG[f] + myristic acid	23	12–56	50	3.5	35
HPC + PEG + AM[g]	21	0–85	150	8.2	69
Gluten + AM	23	0–11	65	5.6–6.6	70
Gluten + oleic acid	30	0–100	50	7.9	22
Gluten + soja lecithin	30	0–100	50	10.5	22
Na-cas[h] + AM	25	0–100	80	18.3–42.5	71
Na-cas + beeswax	25	0–100	104	11.1–42.5	71
W-prot.[i] + palmitic acid	25	0–90	140	22.2	34
W-prot. + stearic alcohol	25	0–86	150	53.6	34
W-prot. + bees wax	25	0–90	170	23.9–47.8	34

[a]T (°C), temperature during transfer.
[b]ΔHR, relative humidity gradient.
[c]l, thickness.
[d]MC, methylcellulose.
[e]HPMC, hydroxypropylmethylcellulose.
[f]PEG, polyethyleneglycol 400.
[g]AM, acetylated monoglycerides.
[h]Na-cas, sodium caseinate.
[i]W-prot., whey proteins.

[5]

Application to fruits and vegetables

Consumer needs increase day by day with developing world. We don't only desire to consume local products but exotics ones on the shelf. Yet, we face a preservation problem considering to transport conditions, as well. In order to increase the shelf-life of the desired product, some classic methods like drying have been being applied for years. Since most of the fruits and vegetables contain more than 80-90% of water, it is importat to preserve that amount of water [12]. There shouldn't be a water vapor transfer.

Fruits and vegetables stored for a long time can be coated with different formulations including paraffin and natural waxes. Additionally, some chemical substances like fungicides or growth regulators can be incorporated. Yet, before distribution to markets and processing these constituents should be removed. This can be done by rinsing or cleaning [13].

Respiration process is another problem beyond water loss. As, it causes carbohydrates to produce carbon dioxide, water and heat, which will lead loss in carbohydrate content. Moreover, it can be seen on their organoleptic properties. There will be changes in their colour, taste and odour. Some researches proved that incorporation of beeswax into chitosan based coatings caused a remarkable decrease in the respiration rate of strawberries [14].

Coatings incorporated with lipids are generally a good solution owing to their stability. However, they can also negatively affect the sensory parameters, leading a waxy sensation. That's why there are still some studies trying to create composite edible films and coatings [15].

Application to meat and meat products

Meat is characterized as a food with tissue structure. Since it has a good source of nutrition with high water content, meat and meat products are prone to microbial spoilage. Especially *Listeria monocytogenes* is one of them. Hydrocolloid coatings based on cellulose derivatives, alginates and gums with addition of acetic or lactic acid or substances showig antimicrobial characteristics can prevent growth of such microorganism [16].

Incorporation of polysaccharide-based or protein-based films with oils is crucial. It may not be benefical always. Vargas, Albors, and Chiralt (2011) studied with chitosan-sunflower edible films with acetic and lactic acid on pork meat hamburgers Studying with chitosan-based films with no oil increased metmyoglobin content of coated hamburgers during cold storage. The addition of sunflower oil to chitosan matrix, on the other hand, caused a reductio in metmyoglobin content. However, it has been observed that the dilution effect of chitosan should be well studied. As, the addition of sunflower oil made an impact on antibacterial effect of pure chitosan films against coliform groups, causing a reduction [17].

Sausages are of great interest because of having remarkable amount of water. Coating with edible film can be a solution as well as vacuum packaging since it helps protect its water content. Some researches produced casings using pectin and gelatin/sodium alginate blends including corn oil and olive oil. The casing was applied using extrusion technology. The results showed that addition of oil enhanced the quality and stability of films [18].

Application to dairy products

Cheese may be the most diverse group in all food products. It can be produced by using starter lactic acid bacteria (SLAB) but it is not a necessity. The shelf-life of cheese which are produced by using (SLAB) has a little bit longer shelf-life comparing to those not produced by using SLAB. Yet, in any way shelf life of most cheese types are limited due to uncontrolled fungal and bacterial development on the surface. Therefore, edible films can be regarded as a way to limit negative changes.

Although it is not as common as in meat products or fruits and vegetables, cheese products somehow find its application area, as well. Ramos et al. (2012) used whey protein isolate, glycerol, guar gum, sunflower oil and Tween 20 with several combinations of antimicrobial compounds like natamycin, lactic acid.

After all, the results indicated that application of these coatings restrict contaminant microorganism and reduces water loss during 60 day of storage [19]. In another study, galactomannan coatings which are plasticized using glycerol containing corn oil reduced 02 consumption and CO2 production rates on semi-hard regional cheese [20].

Application in bakery products

Bakery products such as biscuits, breakfast cereals are desired to have a crispy texture and crispiness is moisture content. Loss of crispiness and getting a soft structure occur with increasing water content.

The water transfer doesn't always occur from surrounding atmosphere to food product but also through the food products. Dried fruits have higher water activiy comparing to cereals. Therefore there will be a water transfer. Talens, Perez-Masia, Fabra, Vargas and Chiralt (2012) studied the effectiveness of edible coatings based on caseinates and chitosan in partially dried pineapple for its use in dry fruit-cereal products. The results exhibited that caseinate-based emulsion coatings prolonged the shelf life of the product [21].

Conclusion

In this review, we discussed the importance of lipids used in edible coating. Lipids, in general saying, are used in edible coating to form a water vapor barrier thanks to their hydrophobic character. Their efficiency depends on several factors including their chemical structure, saturation degree, homogeneity in the film. Although they are mainly used for their water vapor barrier property, some species are used as plasticizers by mainly weakening intermolecular forces between polymer chains. This group includes acetoglycerides, fatty acids, monoglycerides and phospholipids.

Edible films formed with or without lipid have generally lower barrier and mechanical properties.

Comparing to plastic films, yet, considering health and environmental problems emerges an alternative formulations, which is edible films. Their main advantage is that they can be eaten with the food material and they leave no waste behind them. Even if little amount of waste is produced after all, it is completely biodegradable.

Emulsion-based films and coatings have been proven to be effective on increasing stability of a variety of fresh or processed food products. Yet, more research is required to enhance application processes of emulsion based edible materials.

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