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Review

Edible Films: Properties, Industrial Applications and *Salvia Hispanica* as Material for their Development

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Chia is a millenary culture, but with the passage of time, its use fell by the wayside. It was at the end of the last century that the interest in the chia was resurrected. The majority of studies have focused on obtaining and evaluating its oil since it was recognized as one of the best known sources of fatty acids ω -instituted, such as the essential linolenic acids and linoleic acid. However, this seed could be exploited fully since it has good protein level comparable with legumes such as lentils and cereals such as wheat. Also, the amount of fiber is abundant and, to be moisturized, you can retrieve a gelatinous substance called mucilage. The components mentioned earlier (protein and mucilage) can be used as materials for the preparation of edible films, which have the ability to act as a whole to improve the overall quality of many foods (especially the freshness), extend their shelf-life, and improve the mechanical properties and handling, as well as the nutritional characteristics. To determine the purpose of edible films, it is important to evaluate their properties which depend, among another factors, on the type of material used. Thus, the purpose of this review is that the reader knows the nutritive components of chia seed as an alternative to the development of edible films, as well as some variables that influence the formation of films and the most important features by which to evaluate them in order to define the application in the food industry.

Keywords: *Salvia hispanica*; proteins; mucilage; films.

INTRODUCTION

Description of the chia seeds (*Salvia hispanica*).

Another name that is known to Chia seeds (*Salvia hispanica*) is Spanish chia or Mexican chia; these belong to the family Lamiaceae. It is an annual herbaceous plant

of 1.0 to 1.5 m in height, with branched stems of quadrangular section. The flowers are hermaphrodites with a violet tone. As shown in figure 1, the seeds are oval, soft, shiny, and grayish-brown with irregular brown spots in the majority, but some are white and measure between 1.5 to 2.0 mm in length (Ayerza and Coates, 2005). The chia is planted from late spring to early

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Figure 1. Seeds of chia (*Salvia hispanica*)

Table 1.Chemical composition percentage of various grains.

	Proteins	Lipids	Carbohydrates	Fiber	Ash
Rice ¹	6.5	0.5	79.1	2.8	0.5
Barley ¹	12.5	2.3	73.5	17.3	2.3
Oats ¹	16.9	6.9	66.3	10.6	1.7
Wheat ¹	13.7	2.5	71.1	12.2	1.8
Corn ¹	9.4	4.7	74.3	3.3	1.2
Chia ²	23.9	34.8	0.9	35.8	4.3

¹United States Department of Agriculture, (2002); ²Segura *et al.*, (2013).

summer; that is to say, the court of plants starts around four months after planting, according to the maturity state of the same (Beltran and Romero, 2003).

Chia is found naturally in areas of oak forest or pinoencino and distributed in temperate and semi-warm environments of Neovolcanic Axis of the Sierras Mother West, South and Chiapas, at altitudes ranging between 1400 and 2200 m. Historically, this species has been cultivated in both tropical and subtropical environments in frost-free areas and in regions with annual frost, from sea level to 2500 m. It is resistant to diseases and pests and can tolerate low water supply during growth (Beltran and Romero, 2003).

Chemical composition and nutritional aspects of chia seeds (*Salvia hispanica*).

Lipids

The oil content in the chia seed is about 34.8%. Table 1 shows the composition of the seeds and the corresponding data for the five cereals of greatest global significance (rice, barley, oats, wheat, and corn). In the same table, it can be seen that the content of proteins, fats, fiber and energy of the chia seed is greater than in other crops.

The oil from chia seed, is rich in ω -3 and ω -6 fatty acids, primarily the linolenic acid and linoleic acid, as can be

Table 2. Composition of fatty acids in chia (*Salvia hispanica*) seeds

Fatty Acid		Fatty acid (%)	
		Jménezet al. (2013)	Nitrayova et al. (2014)
Myristic	C14:0	0.08	0.06
Palmitic	C16:0	7.29	7.04
Palmitoleic	C16:1	0.06	0.03
Hexadecadienoic	C16:2	0.18	NR
Stearic Acid	C18:0	3.84	2.84
Oleic acid	C18:1	8.91	7.30
Linoleic Acid	C18:2	19.36	18.89
Linolenic acid	C18:3	51.82	63.79
Arachidonic Acid	C20:0	0.23	0.02
Gadolenic	C20:1	0.12	NR
Eicosadienoic	C20:2	0.28	NR
Behenic	C22:0	Traces	NR
Docosatetraenoic	C22:4	Traces	NR
Lignoceric acid	C24:0	Traces	NR
Relation ω -6: ω -3		0.29	0.3

Table 3. Comparison of the fatty acid composition in various sources.

Type of fatty acid (% of total)	Fatty acid composition					
	Oleic acid	Linoleic Acid	Linolenic acid	Myristic	Palmitic	Stearic Acid
Chia	6.5	19.0	63.8	-	6.9	2.8
Linseed	19.5	15.0	57.5	-	5.5	1.4
Algae	5.4	2.3	1.7	4.2	14.5	0.8
Menhaden	25.0	2.2	29.8	8.0	15.2	7.8

Ayerza and Coates (2005)

seen in table 2. The former can be transformed into eicosapentaenoic acid (EPA), desaturases and elongases and subsequently into docosahexaenoic acid (DHA). In turn, the latter is derived in arachidonic acid or AA (Knoch *et al.*, 2009). The AA, EPA and DHA are important structural components of the phospholipids of cell membranes and are the substrates for the formation of a number of lipid derivatives. Linolenic acid, a precursor of DHA, has low availability in the diet, with its consumption in some populations being very restricted. Currently, the changes in feeding patterns have led to the increased consumption of vegetable oils that are rich in linoleic acid (ω -6), which is why the relationship ω -6: ω -3 is of the order of 15:1 in many countries, when the ideal ratio is 5:1 or 10:1 (FAO/WHO, 1994). Due to the high content of ω -3

fatty acids and the ω -6: ω -3 relation, the oil from chia seeds is a good alternative for incorporation into human food (Jimenez *et al.*, 2013).

Of all of the sources of ω -3 fatty acids, only linseed (*Linum usitatissimum*) and chia have their origin in agricultural crops. Both are plant species with the largest concentration of fatty acid linolenic acid known to date (Table 3). These seeds are often used as a food ingredient, mashed, or in a natural form as a dietary supplement. The other two available sources are of marine origin: algae and menhaden fish oil (*Brevoortia tyranus*) (Ixtaina, 2010).

When comparing the composition of the oil of the four sources, it can be seen that the land sources have much higher ω -3 contents than those of marine origin, which

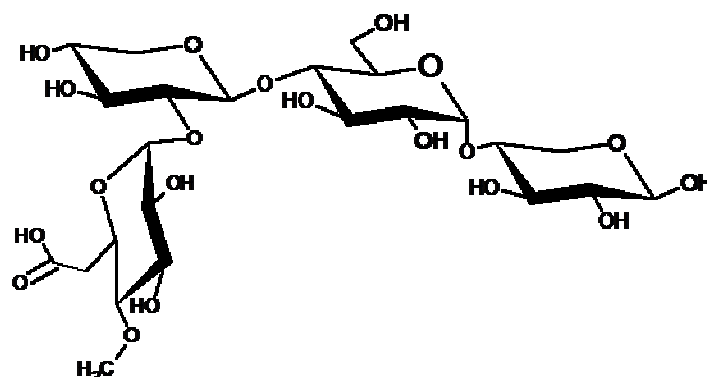


Figure 2. Structure that comprises chia (*Salvia hispanica*) mucilage

represents a very important advantage for the sources of seaweed and fish, because they contain a quantity of saturated fatty acids (myristic, palmitic and stearic acids) that is significantly lower. Another advantage is that the oil obtained from the chia seed does not produce a fishy odor, so that the products obtained or made from the chia seed do not require packaging and special storage conditions to prevent even the smallest changes caused by the environment; therefore, the natural antioxidants have replaced the use of artificial stabilizers (Ayerza and Coates, 2005).

Fiber

It should be noted that the fiber is one of the most abundant components in Chia seeds, where it is found at a level of 35.8% (Segura-Campos *et al.*, 2013). Vazquez *et al.*, (2015) obtained a fraction that is rich in fiber from chia flour, with total dietary fiber contents of 56.5%; of this, 53.5% corresponds to insoluble fiber and only 3.0% to soluble fiber. Taking this into account, the fiber-rich fraction of the chia flour could be incorporated as an ingredient in the development of dietary physiological products. The consumption of dietary fiber from insoluble types is considerably related with a feeling of satiety due to its ability to absorb water; the fiber occupies a space in the stomach and decreases the need to ingest food, also causing an increase in the volume and weight of the fecal mass which is reflected in the improved functioning of the digestive system and reduction of ailments like constipation. It is recommended for the treatment of irritable bowel syndrome, and for problems such as diverticulitis and colon cancer (Ayerza and Coates, 2005).

Craig and Sons (2004) reported that once the oil has been extracted from the chia seed, the remnant material

contains a high content of fiber (33.9%), approximately 3-5% represents a mucilaginous fraction that behaves physiologically as soluble dietary fiber, while the rest (30.4%) corresponds to insoluble fiber.

The chia mucilage is a high molecular weight polysaccharide, which varies between 0.8 and 2×10^6 Da. The same emerges from the seed when it enters in contact with water, covering it in the form of a transparent halo. The structural units that make up the mucilage of the chia seed have been described as a tetrasaccharide with a **main chain composed of units of (1→4)-β-D-xylopyranosyl (1→4)-α-D-glucopyranosyl** with ramifications of 4 methyl-α-D-glucuronic acid in the O-2 position of β-D-xylopyranosyl from the main chain (Figure 2). The relationship of the monosaccharides β-D-xylose, α-D-glucose and 4-O-methyl-α-D-glucuronic acid is 2:1:1. It should be noted that the content of glucuronic acid is high (approximately 25%), which is characteristic of this type of substance (Lin and Daniel, 1994).

Chia mucilage has high viscosity in water with possible beneficial metabolic effects with respect to other sources of dietary fiber from lower viscosity, such as guar gum. The existing information in terms of their function properties indicates that this is a polymer with thickener action. The mucilage obtained from the fiber rich fraction, is capable of retaining more than 100 times its weight, absorbs 44.08 g and adsorbed 0.27 g of water per gram of gum. Its capacity for oil retention is 25.79 g water (Segura-Campos *et al.*, 2014). In a previous study (Muñoz, 2012), the high solubility of mucilage in water at different temperatures (30, 60, 70 and 90°C) and concentrations (0.15, 0.25 and 0.5%) was demonstrated; this gives a potential industrial applicability, because mucilage with higher solubility is considered to be of higher quality. In addition, due to its affinity for water and

the capacity to dissolve or disperse in it, mucilage can be used in the development of biodegradable films (Quintero *et al.*, 2010).

Protein

Compared to other seeds and grains, chia provides a high source of protein representing 23.9% of its weight. Its content is similar to that of lentils (23.0%) and chickpea (21.0%) and higher than the protein content of grains such as commonly used corn (10.0%), wheat (14.0%), rice (8.0%) and oat (15.3%) (Lazcano and Cuellar, 2004). Levels of up to 28.4% have been reported for others chia varieties; these values justify the potential use of seed as a source of protein for human diets and animals. In addition, the chia seed presented advantage that it does not contain gluten, which is why it has been approved by the celiac Association Argentina as suitable for use in celiac patients (Ayerza and Coates, 2006). Olivos *et al.*, (2010) stressed that the chia protein has important physicochemical characteristics, such as a good water-holding capacity and an excellent retention capacity of oil, which is relevant for use as functional additive in bread industry and in production of stable emulsions.

In a study performed by Vazquez *et al.*, (2015), the fractionation was obtained based on the solubility of a protein-rich portion of chia (Globulins: 64.8%, glutelins: 21.2%, albumins: 10.9% and prolamins: 4.04%). Sandoval (2012) found that for chia, the major fraction corresponds to globulins, accounting for 52%, followed by albumins with 17.3%, a lower proportion of glutelins (14.3%) and the prolamins with 12.7%. The last author obtained a higher proportion in the albumin fraction, which could be due to factors such as the particle size of the flour, the force of agitation, the flour-solvent relationship, the number of extractions by stage, as well as the physiological status of the seed, all of which can influence the proportion of the different fractions.

The denaturation temperatures in the protein fractions of chia (Sandoval, 2012) have been reported to have values of 103.6°C for albumin, 104.7°C for globulins, 85.6°C for prolamins and 91.3°C for glutelins. They can be considered high in relation to those reported for other vegetable proteins. For example, denaturation temperatures for proteins of rice are below 100°C (Ju *et al.*, 2001) and those of the amaranth seed are between 64 and 94°C (Salcedo *et al.*, 2002). The high denaturation temperatures could indicate that the shape of the components of these fractions is stabilized by a large number of hydrophobic interactions, which are naturally endothermic and, therefore, require a greater amount of energy for denaturation. Similarly, these high

temperatures show enhanced thermal stability, which is important in the field of food because the proteins support high temperatures without losing their native three-dimensional structure, or functional or biological activity, thus having practical applications in the food industry (Sandoval, 2012). The composition of amino acids in the chia protein, once the flour of this seed is defatted, is shown in table 4. This has also been shown by comparison of the amino acids of the chia seed with the requirements of aminoacids for adults proposed by the FAO/WHO/UNO (2011). The defatted flour contains sulfur-containing amino acids, cysteine and methionine, in high proportions (32g/kg of protein), as well as the aromatic aminoacids (phenylalanine, tyrosine and tryptophan) in greater amounts (84 g/kg of protein). The lysine content is similar to that which is recommended and shows a significant amount of non-essential amino acids such as aspartic acid and glutamic acid. With regard to the *in vitro* digestibility of the protein-rich fraction of chia, a value of 77.5% has been reported (Vazquez, 2015), which is higher than that found for chickpea flour, with 75.2% (Sánchez *et al.*, 1999), and for fishmeal Lima bean (*Phaseolus lunatus*), with 72.4% (Betancur *et al.*, 2004). There are no reports of non-nutritional factors in the chia, with which you can rule out the presence of protease inhibitors that could retard the *in vitro* digestibility (Siddhuraju and Becker, 2001).

Vitamins and minerals

The chia seed is a good source of B vitamins (Table 5). Recent research has shown that low levels of vitamin B in the blood is associated with an increased risk of fatal coronary heart disease and stroke. Comparison of the vitamin content of chia compared to other traditional crops shows that the level of niacin (vitamin B3) is greater than that in corn, soybeans and rice. The concentrations of thiamine (vitamin B1) and riboflavin (vitamin B2) are similar to those of rice and corn, although they are lower than those of soybean (Ayerza and Coates, 2005).

With respect to the minerals content, chia seeds are an excellent source of calcium (631 mg/100g), phosphorus (860 mg/100g), magnesium (335 mg/100g), potassium (407 mg/100g), iron (7.72 mg/100g), zinc (4.58 mg/100g) and copper (0.924 mg/100g). In addition, they contain between 13 and 354, 2 and 12 and 1.6 and 9 times more calcium, phosphorus and potassium, respectively, than wheat, rice, barley, oats, and corn (USDA, 2002). The levels of iron in the chia seed and defatted flour are very high, introducing values that are not frequently seen in seeds.

Table 4. Amino acids composition in defatted chia (*Salvia hispanica*) flour

Essential amino acids	(g/kg of protein)	
	Defatted flour	FAO/WHO/UNO
Lysine	50.0	45.0
Tryptophan	9.5	6.0
Phenylalanine	51.5	38.0 ^B
Tyrosine	23.0	
Methionine	13.0	22.0 ^C
Cysteine	19.0	
Threonine	39.0	23.0
Leucine	72.0	50
Isoleucine	33.0	30.0 39.0
Valine	46.0	
Non-essential amino acids		
Aspartic Acid	102.5	
Glutamic Acid	199.5	
Serine	64.5	
Histidine	25.5	
Arginine	102.5	
Alanine	51.0	
Proline	40.0	
Glycine	59.0	

At the request for adults

B aromatic amino acids: Phenylalanine Tyrosine + + Tryptophan

C Amino Acids: Cysteine + Methionine Vázquez, (2007).

Table 5. Vitamin content of Chia seeds (*Salvia hispanica*).

Vitamins	Content (mg/100 g)
Vitamin C (ascorbic acid)	1.6
Thiamine	0.62
Riboflavin	0.17
Niacin	8.83
Folate	0.049
Vitamin A	54 UI
Vitamin E (alpha-tocopherol)	0.5

National Nutrient Database for Standard Reference (USDA) (2002)

UI: international Units

Antioxidants

Extracts of water and methanol of chia seed after it has been pressed and the oil has drained have shown a strong antioxidant activity. Chlorogenic acid (7.1×10^{-3} mol/kg

chia) and caffeic acid (20.1×10^{-3} mol/kg chia) are the most important antioxidants in the chia seed. Their importance lies in the protection against lipid oxidation that affects both the quality of the food and the health of consumers, with the possible deterioration of the organoleptic, functional and nutritional characteristics.

These antioxidant properties are significantly stronger than those of ferulic acid and those of the common antioxidants such as vitamin C (ascorbic acid) and vitamin E (α -tocopherol) (Reyes *et al.*, 2008). Also, it has been found that the seeds contain flavonols such as quercetin and kaempferol, all contributing to the strong antioxidant activity (Beltran and Romero, 2003). Some research has shown that quercetin is a potent antioxidant that can prevent the oxidation of lipids, proteins and DNA and their properties are significantly more effective than the non-orthohydroxy flavonols (Korhonen, 2009).

Potential uses of chia seeds (*Salvia hispanica*).

Chia is an attractive non-conventional crop that has great potential to be exploited and can serve to replace traditional crops that are not profitable in the country; one of the most important uses of this seed is the production of oil, which has the advantage of containing a large amount of essential oils. The main application of this product is in the production of capsules that provide a nutritional supplement of ω -3. It is also possible to extract oil from the leaves of chia, which can be consumed as a condiment or used as a fragrance (Beltran and Romero, 2003).

At the international level, the Food and Drug Administration (FDA) consider chia seed to be a dietary supplement. On the other hand, in 2009, the marketing of chia seeds and crushed chia seeds to be used as a novel food ingredient in bakery products was authorized in the community market (European Union), with a maximum content of seeds of 5% (Commission of the European Communities, 2009).

Studies (Guevara and Aguilar, 2012) have suggested the importance of considering the incorporation of the whole chia seed to the usual diet as a complement to other foods, not only because of the high protein level and quality of the same, but also due to the hypolipidemic properties, which makes it a beneficial food for health. Also, chia is ideal for the enrichment of certain foods due to its ω -3 fatty acid content, its good source of fiber, its protein content and the level of antioxidants in its flour. The most common products which have incorporated this seed are: bread with chia, breakfast cereals and crackers, as a nutritional supplement, baby formula, food for animals, nutrition bars, and other less common foods such as yogurt, biscuits and tortillas.

Another application of chia seeds was identified by Segura-Campos *et al.*, (2016) who focused on obtaining material (mucilage) for the development of capsules and edible films. For the formation of capsules, chia mucilage and a mixture of chia mucilage with sodium alginate in a

ratio 50:50 were employed to a concentration of 1%; the diisocyanate agent that was used was 0.3 M calcium chloride. The result was that only the mix of mucilage of chia with sodium alginate had capsule-forming capacity. For the preparation of films, dispersions were prepared at a concentration of 1%, using glycerol as a plasticizer up to 20 and 40% of the weight of the gum. It was placed in petri dishes with a diameter of 10 cm and were left dry in an oven with air circulation of 30°C for 24 h. It was noted that the films developed with 20% glycerol proved to be the most resistant to requiring greater tensile strength (1.21 and 0.76 kgf/mm²) to break; the deformation percentage (12.55-16.68%) was higher for films with 40% glycerol, as was the elasticity (Young's modulus: 2.4 kgf/mm²). The properties analyzed in this study allow the usefulness of the films to be determined, either as a coating or as packaging, which is how this will be used. However, it is also important to identify the optimal conditions to obtain films with better properties (strength, flexibility, permeability adequate) in such a way that can be used for the coating of foods such as fruits, vegetables, meats, and cheese, among others (Campos *et al.*, 2011).

Biodegradable Materials

At present, due to the growth of sustainable production, materials are being searched for so that packaging can be made with the least possible impact on the environment. As a response to this need, biodegradable materials arose, which are a valid alternative to the use of the traditional plastics that are derived from petroleum (a non-renewable natural resource) and require a time of approximately 200 years to be incorporated again in nature (Parzanese, 2011).

Biodegradable materials are those which, when exposed to certain conditions of humidity, microbial flora and oxygen over a period of several months, are transformed into simple substances (mainly water and carbon dioxide) and biomass by the enzymatic action of microorganisms (bacteria, fungi and other) present in the environment. The structural units of the materials of this type are called biodegradable polymers and are derived mainly from renewable raw materials of animal, plant or microbial origin, but are also generated synthetically from petroleum products. These biodegradable materials are currently used in various sectors (medicine, agriculture, food, packaging, among others) taking into account the functional characteristics that must be present in the material according to the specific application for the intended purpose (Robertson, 2006). In the area of food, these polymers are applied in the manufacture of biodegradable packaging (mono and multilayer),

Table 6: Applications of the edible films

Purpose	Application
Provide an individual protection against moisture and oxygen.	Fresh fish, cheese, meat and meat products.
Delaying the external microbial growth.	Intermediate moisture foods.
Check the moisture balance within a heterogeneous food.	Pizzas, pays, sandwiches, pastries.
Improve the mechanical properties.	Peanuts, shrimp, snacks.
Provide structural integrity to strengthen the structure of the food.	Restructured Meat, fish, freeze-dried food.
Restrict the migration of moisture.	Fruit, baked goods, frozen.
Protect the parts that will be within cups or bags.	Cheeses, frozen and ice cream.
Protect the surface or the baling of fat absorption.	Cubes of cheese, dried fruit, snacks, frozen.
Improve the appearance of the food by adding brightness.	Baked Goods, fruits, snacks.
Providing or improving color, odor, flavor and palatability.	Various food.

Parzanese (2010)

packaging assets, edible films and edible coatings (Parzanese, 2011).

Edible Films and their application in the food industry

The development of films consists of the formation of thin layers that act as a barrier between a product and the environment that surrounds it. These are used as a protective coating of nutrients, flavors and certain foods that have to be transported or stored, avoiding the migration of moisture and lipids (Quintero *et al.*, 2010). In table 6, examples of the use of edible films in the food industry are listed. In many applications, the most important function of the films is a reduction in moisture loss, due to the fact that it must maintain certain levels of water activity (A_w) because this is a vital factor in the quality and safety of the food.

Some films and coatings have been applied to control the transfer of certain gases (oxygen, carbon dioxide, etc.) in such a way that an ideal atmosphere that delays deterioration will be generated within the packaging. This atmosphere varies depending on the type of food; in fruits and vegetables, semi-permeable films and coatings are used; that is to say, they have some oxygen permeability, because the extremely waterproof wraps can induce the creation of an anaerobic environment that causes undesirable changes in this type of product, such as a loss of aroma. On the other hand, films that are impermeable to oxygen are applied, especially in high-fat food (blue fish, dried fruits, etc.) since the quality of these products mainly decreases by lipid oxidation. Fat oxidation generates compounds with unpleasant flavors (musty

taste) or undesirable odors. In this sense, Lee and Krochta (2002) and Lee *et al.*, (2002) reduced the oxidative rancidity of the peanuts and, therefore, increased their life through the use of coverage on the basis of whey proteins.

An application studied extensively is the use of edible films spiked with antimicrobial agents to protect foods from the risk of **microorganism's** growth and, therefore, prolonging the shelf life of the same (Campos *et al.*, 2011). Such is the case of edible film applications in minimally processed fruits and vegetables (Bourlieu *et al.*, 2009). In fruits specifically, the films of sodium alginate have been studied in order to slow down the deterioration of chilled peaches and strawberries (Moayednia *et al.*, 2009). The shelf life of refrigerated apples, cucumbers and tomatoes treated with starch films spiked with potassium sorbate has also been studied (Mehyar *et al.*, 2011). Similarly, the films of carboxymethyl cellulose help to prolong the shelf life of chilled cherries and green peppers (Lim *et al.*, 2011).

The collagen-based wrap probably represents one of the edible films with the most commercial success from the commercial point of view, since they are used as substitutes for the natural sausage casings in the manufacture of meat products and type of sausage. These wrappers are primarily used to maintain the structural integrity of the meat products (Chapman and Potter, 2004), but also have other beneficial functions such as delaying moisture loss, lipid oxidation, discoloration, improving the appearance of the product or as a bearer of food additives (Veronique, 2008).

One of the advantages of edible films is the fact that

they can serve as vehicles of other ingredients with a specific purpose, as has been incorporated in formulations of antimicrobial agents, flavors, antioxidants and pigments. A study was performed by Avila *et al.* (2010), with the objective of the use of essential oil of oregano in the preparation of edible films made of amaranth, chitosan and starch to assess inhibition of *Aspergillus niger* and *Penicillium* spp. Another case is the work of Lopez (2010), where biodegradable films were developed from mixtures isolated from whey protein and native starch of potato and the antioxidant properties due to the incorporation of phenolic extracts of tamarind (*Tamarindus indica*) were assessed.

The formation of films and their properties is due to the interaction of molecules in a disorderly manner, which is dependent on the space they occupy, or ordered structures that form stable associations within a compact network (Villagómez *et al.*, 2008). Its elaboration should be regarded as the type of component which will be used and the factors involved in the process such as the type of solvent, the technique used, the pH value of the film-forming solutions, the use of plasticizers that have a function of increasing the flexibility of the films, and the use of protein constituents, polysaccharides or lipid that can influence the water vapor permeability.

Materials for the training of edible films

Depending on the type of biopolymers (proteins, polysaccharides or lipids) composing the film, its features and functions will be different, since they are linked to the chemical and structural composition of the biopolymer.

Polysaccharides, proteins and lipids have been used as raw materials in the manufacture of edible films (Cisneros and Krochta, 2002). However, the materials developed with a single component present poor barrier and/or mechanical properties, depending on the type of biopolymer used. To counteract these shortcomings, it is necessary to use mixtures of 2 or more components with the aim of improving the properties and characteristics of the resulting material (Diab *et al.*, 2001).

Polysaccharides

They are widely used in the food industry as stabilizers and thickeners. These produce a substantial increase in the viscosity and in some cases have gelling effects because they dissolve and disperse readily in water (Parzanese, 2010). Due to their filmogen properties, these compounds can also be used in the manufacture of envelopes or edible films. In general, they produce films with good mechanical properties and are effective barriers

against compounds of low polarity. However, their hydrophilic nature results in low resistance to water loss; in other words, it has the disadvantage of permitting the transport of moisture. This type of film is not greasy and low calorie. Its selectivity in terms of permeability to oxygen and carbon dioxide constrains the creation of modified atmospheres in the interior of the food without the high risk of developing anaerobic conditions, which translates into an increase in the life of the product (Parra *et al.*, 2004), as well as providing effective protection against the oxidation of lipids and other food components (Flores, 2007).

Among the most common polysaccharides that are used for the formation of films are:

Alginates

This polysaccharide is present in algae as a structural component of the cell wall, in a manner similar to cellulose and pectin in the cell wall of plants on land. Alginic acid is insoluble, but its salts of alkali metals are soluble in water and form gels rapidly in the presence of calcium, which have good characteristics to be used as edible films (Martin, 2005). These films are impervious to fats and waxes, but allow the passage of water vapor. These have been used to preserve minimally processed foods such as fish-based products, which contain oil with a tendency to rapid oxidation, even when they are frozen. If the fish is frozen with a coating of calcium alginate, this will be protected from air, and will therefore show reduced tendency to oxidation.

In an investigation by Wu *et al.*, (2001), the effect of film type on the loss of moisture and oxidation of lipids was assessed in ground beef for burgers with 20% fat, during 6 days of storage at 4°C. The films prepared were: mixtures of alginate-starch (1 and 2.5% w/v) (AA) and mixtures of alginate-starch (1 and 2.5% w/v) with stearic acid (20% p/p of the alginate and starch) (AAA). The ability of these films to transport and distribute tocopherols in the surface of the meat for hamburgers was also evaluated by means of comparing the reduction of lipid oxidation between the treatments with edible films. It was found that the AAA mixture was the more effective in controlling moisture loss (AAA = 16% and AA = 19%) than in the reduction of the lipid oxidation (AAA = 6 and AA = 6.5 mg malonaldehyde/kg of meat). By adding tocopherols (2 g), the films were more effective at inhibiting the oxidation of lipids in comparison with those that were not (AAA with tocopherols = 5.6 and AA with tocopherols = 5.5 mg malonaldehyde/kg of meat). Most of the edible films evaluated were not as effective in slowing the loss of

moisture and the oxidation of lipids in comparison with the use of polyester vacuum bags.

Moraes *et al.*, (2012) developed a study whose aim was to assess the physical and chemical parameters of the Williams pear, stored at 25°C for 15 days, with and without an edible coating. These coatings were prepared with 2% alginate (RA) and 0.5% carrageen (RC). The analyses performed on the samples were: loss of weight, pH, soluble solids, firmness and color. The edible coatings were characterized in terms of mechanical properties, permeability, thickness and opacity. The results showed that the application of edible coatings with carrageenans and alginates in pears influenced the physical and chemical characteristics when compared with the control (uncoated). The weight loss of the control was higher (11%) compared with samples RA = 7% and RC = 8% and the firmness of the fruit with RA (6.5 N) was greater than the control with 1.5 N, and RC with 1 N. However, the coating of alginate showed the best results in the conservation of pear since it had lower permeability to water vapor (3.42×10^{-7} g/MPa.h) and a greater force to the tensile strength (60.95 MPa).

Starches

Chemically, starch is formed by glucose polymers by united glucosidic α (1-4) and α (1-6) linkages, giving rise to two basic fractions, amylose and amylopectin. In most of the cereals, the starch contains 75% amylopectin and 25% amylose. Due to its abundance and low cost of production, there is great interest in the use of starch as a component of edible films and biodegradable coatings. The films produced on the basis of this carbohydrate are clear, flexible, and transparent and are excellent barriers to oxygen (Rojas *et al.*, 2009). However, its barrier properties against moisture are not so good (Joaqui and Villada, 2013). In addition, the mechanical properties are generally lower than those of synthetic films. In films based on starch, the matrix, or network is typically formed during the drying of a gelatinized dispersion due to the hydrogen bridges that are established between the hydroxyl groups (Tapia *et al.*, 2005).

Starches from different sources such as potatoes, corn, wheat, rice, and yuccas, both natural and modified, have been used in the manufacture of edible films. For example, Parra *et al.* (2004) obtained films of cassava starch (1 g of starch/100 ml water) mixed with glycerol (1, 2 and 3 g), glutaraldehyde (0.1, 0.2, 0.3 and 0.5 g) and polyethylene glycol (0.1, 0.2 and 0.3 g) as plasticizers. These films were prepared in order to determine the mechanical properties and water vapor transmission. The results showed that the films made with cassava starch

and up to 0.3 g of polyethylene glycol exhibited good elongation or flexibility (52.1%). However, the formulations with levels above 1 g of glycerol increased water vapor transmission (until 9.03×10^{-7} g H₂O.mm/h.cm²), reducing the application of these films in humid environments.

For its part, Tapia *et al.* (2005) developed films with amaranth flour to 4% using glycerol (25, 30 and 35%) as plasticizers. The films presented an elongation of the break-up of 83.74 % and Young's modulus of 215 MPa. However, the permeability to water vapor (PVA = 0.025×10^{10} g/m.s.Pa) and oxygen (PO = 0.00065×10^{10} cm³/m.s.Pa) were lower than those presented in films by other polysaccharides such as starch from maize (PVA = 2.57×10^{10} g/m.s.Pa and PO = 4.61×10^{10} cm³/m.s.Pa) and proteins as whey (PVA = 2.57×10^{10} g/m.s.Pa and PO = 4.61×10^{10} cm³/m.s.Pa.).

Chitosan

This high molecular weight polysaccharide, normally achieved by alkaline deacetylation of chitin and from crustaceans, is widely used as edible coating. Edible films made from chitosan are effective in prolonging life and improving the fruits quality, delayed ripening, regulation of the respiratory rate, reduction of dehydration, a decline in the loss of sweating, modification of the internal atmosphere, etc. (Martin, 2005).

In the same way, chitosan offers potential for applications in the food industry because of their individual physicochemical properties, rapid biodegradability, antimicrobial property, antifungal activity and non-toxicity. In this way, the chitosan-based films have attracted attention in the conservation of food and in packaging technology. This is mainly due to the fact that the films of chitosan have antimicrobial activity against pathogenic microorganisms and of deterioration, including fungi and both Gram positive and Gram negative bacteria (Aider, 2010).

Aguirre *et al.*, (2013) made films with chitosan (7, 10 and 15 g/L), oleic acid (0, 3 and 6 g/L) and glycerol as a plasticizer (10 g/L), which were characterized according to physical properties such as color, solubility in water, permeability to water vapor and oxygen permeability (PO₂), with the purpose of expanding knowledge about the functionality of this type of film. The incorporation of oleic acid limited the transfer of water vapor in the films developed with 15 g/L of chitosan, probably due to the viscosity of dispersions ($\eta = 2.07$ Pa.s) that promoted the stabilization of emulsion during the drying of the film. The incorporation of oleic acid did not generate significant changes ($p > 0.05$) in the values of PO₂ of the films and these showed a slight yellow-green.

In another study by Sebtí *et al.*, (2007), the use of chitosan (1% w/v) and nisin (250 µg/mL) as raw materials in the production of films was raised. It was shown that even low concentrations of chitosan (1% w/v) were sufficient for the total inhibition of *Aspergillus niger* and *Kocuria rhizophila* (pre-cultured for 5 days at 30°C) microorganisms that deteriorate the food. Measurements of the tensile strength (18 MPa), as well as elongation (61.5%), showed that the chitosan films were elastic and flexible. The transfer of water vapor (1.2×10^6 g/m.d.Pa) as well as the ranges of water desorption (2×10^6 kg/m².s), suggested that the films of chitosan were slightly sensitive to water. The transfer of water was reduced by 60% in comparison with other films of biopolymers.

Cellulose Derivatives

The cellulose and especially its forms such as carboxymethyl cellulose (CMC), methylcellulose (MC), hydroxypropyl methyl cellulose (HPMPC), and hydroxypropyl cellulose (HPC), among others, are considered good bulking agents of films, because they are capable of forming continuous networks in aqueous solutions (Turhan and Sahbaz, 2004). HPC is the only truly thermoplastic polymer, so it can be extruded, cast or molded to form films. Generally, the films formed from these esters are strong, clear and resistant to oils and the majority of non-polar organic solvents. This type of cover is used to control the spread of oxygen and carbon dioxide with the purpose of delaying the process of ripening fruits and vegetables. Although the barrier properties to the humidity of the films from cellulose are not very good, these can be improved with the addition of hydrophobic substances (Pérez and Báez, 2003).

Carrasco *et al.*, (2002), evaluated the effect of edible coatings of carboxymethyl cellulose to 1% and 0.25 g of stearic acid added with 0.5 ml of glycerol, on green peppers (*Capsicum annuum*, L) to determine its effect as a protective agent and stabilizer of the natural characteristics of the fruit. The results showed that the coatings based on carboxymethyl cellulose and lipids were effective to reduce the deterioration of peppers by floppiness and wilting during storage (25 days) when compared with the control (uncoated); that is to say, the reason for the change in firmness during storage in the control (RCC) was 3.8 and coated (RCR) was 2.8. In addition, the coated peppers had a significantly lower loss of sensory quality total (RCC = 3.2 and RCR = 2.4) and appearance (RCC = 3.8 and RCR = 2.8), as well as a lower weight loss (0.68g/day) in comparison to the fruit without a coat (1.20 g/day).

In another study, coating formulations were made using

1, 5, 3, and 4.5% (w/v) hydroxypropyl methylcellulose as a support matrix, to which three non-ionic surfactants (sorbitan monooleate, sorbitan monolaurate and mono diglycerides of fatty acids) were added to the 3% p/v; this is commonly used in food with the goal of enhancing the property of barrier to water vapor (PVA) and the adhesiveness of the coatings on the surface of products such as strawberries. The PVA films ranged between 15 and 42×10^{10} g/Pa.s.m. The lower values of PVA (15×10^{10} g/Pa.s.m) were obtained with the highest proportion of polymer in the film and with the surfactant polyoxyethylene sorbitan monooleate. It was concluded that, for surfactants and the quantity used (3%), there is a need for a critical concentration of polymer to be a significant improvement in the resistance to the transfer of water vapor (Pastor, 2010).

Mucilages

These are types of soluble fiber; in contact with water, they are viscous solutions or swell in them to form a gelatinous mixture (Malviya *et al.*, 2011). There are few studies about the use of the mucilage as an ingredient for the formation of edible films, including the use of the nopal mucilage (Gonzalez, 2011) and chia (Segura-Campos *et al.*, 2016). González (2011) focused on the development and evaluation of a film made from a solution of prickly pear mucilage (*Opuntia ficus-indica*) to the 1% p/v, using glycerol, polyethylene glycol and oleic acid as plasticizers to coat prickly pear and increase the shelf life. A methodology was developed to obtain dehydrated mucilage for prickly pear with characteristics that would allow the homogeneous dispersion of the same to rehydrate during the formulation with the plasticizers. Three formulations of edible films were tested: APG (mucilage solution, 1.5% glycerol, 1.5% polyethylene glycol, 0.1% oleic acid); BPG (mucilage solution, 5% glycerol, 5% polyethylene glycol, 0.3% oleic acid); and CPG (mucilage solution, 3% glycerol, 3% polyethylene glycol, 0.5% oleic acid). Determinations were carried out by batches of respiration rates of prickly pear vegetables, obtaining reductions of up to 92.6% with the coatings. The results of the measurement of water vapor permeability to the films with different formulations were similar: APG = 77.96, BPG = 84.15 and CPG = 84.56 g.mm/kPa.m².day. The film thickness was greater with CPG, with a result of 0.256 mm.

Segura-Campos *et al.*, (2016), extracted the mucilage of crushed and whole chia seeds by a process of defatting, hydration, solubilization, filtration, dehydration and

spraying. The proximate composition and some functional properties of mucilage were assessed and its feasibility for the development of films was determined. The mucilage presented high water retention capacity, more than 100 times its weight in water, high water absorption capacity (62.64 -143.66 g of water per gram of gum), and was able to adsorb 0.69-1.35 g of water, presenting higher capacity than the mucilage obtained from whole seeds. The films were formed by adding 20 and 40% glycerol to mucilage dispersion, obtaining films with a thickness between 0.08-0.11 mm, reaching a maximum tensile strength of 1.21 and 0.76 kgf/mm² for the films with 20% glycerol, while those containing 40% presented a higher deformation percentage (12.55-16.68%). The films of chia showed a high affinity for water and its protein content provided thickener, stabilizer and emulsifier properties that could be exploited for the improvement of food products.

Proteins

Natural polymers such as proteins offer a great opportunity to be used as raw material for the production of edible films due to its biodegradability and the fact that it can supplement the nutritional value of food. In addition, it confers to the films a wide range of properties due to the potential to form intermolecular links. Due to the different structural conformation levels that can be present in the protein structure (primary, secondary, tertiary and quaternary), films can be formed with a high degree of cohesiveness, which is stabilized when new links or interactions are formed. Within the vegetable-based proteins that have been used for training of films are the following:

Casein

Caseinates are good trainers of emulsified films due to its amphiphilic nature, its disorderly structure and their ability to form hydrogen bridges. The films of caseinate presented favorable characteristics for its use in food products such as transparency and flexibility (Parzanese, 2010). However, the films of casein proteins present several problems in their characteristics. In the first place, the films are highly sensitive to moisture. They easily absorb and release water molecules, which act as a plasticizer and greatly affect the mechanical properties of the film. Secondly, the films of casein prepared with glycerol are unable to provide high mechanical resistance and high elasticity, as are the synthetic films. Thirdly, its relatively high cost, limited use as a raw material and the complex procedures to generate it can cause problems in processing (Han and Gennadios, 2005; Dangaran *et al.*,

2009). A number of studies have been performed to try to solve these problems. Dangaran *et al.*, (2006) developed a method for the precipitation of hydrophobic casein through processing of high pressure with CO₂. With this, a casein with lower solubility in water was obtained and the films developed were less susceptible to high-humidity environments. To improve the appearance, the size of the protein particles was reduced in the elaboration of laminating films with glycerol. The result was a film with more brightness, greater surface tension and lower permeability to water vapor. Another study to improve the properties of casein was performed by Rezvani *et al.*, (2013) who used stearic acid (0-2 g/100 g) as an additive in the formation of films with sodium caseinate (6-8 g/100 g). Changes in the proportions of sodium caseinate and stearic acid with respect to water had a significant effect on the permeability to water vapor and surface tension. The highest values of consistency coefficient and elastic modulus were obtained in the presence of stearic acid in the highest concentration. The edible film prepared with 6 g/100 g of sodium caseinate and 2 g/100 g of stearic acid showed lower vapor permeability, below 1.36 g.mm/m².h.kPa. This study was useful to improve the water resistance and mechanical properties of the films of casein prepared with stearic acid.

Another protein, gelatin, was used to improve the mechanical resistance, as well as the barrier properties of water vapor. In a specific case (Chambi and Grosso, 2006), intercrossing of transglutaminase was used to produce edible films of casein, gelatin and mixture of casein-gelatin (100:0, 75:25, 50:50, 25:75 and 0:100). The casein-gelatin film showed significantly higher values in elongation with or without the treatment of transglutaminase (55 and 33%, respectively), compared with the films made from gelatin or casein alone (15 and 10%, respectively). Mixtures of casein and gelatin produced a synergistic effect observed only in the elongation of film. The improvement was detected to the tension force and barrier properties of water vapor, in the mixture casein:gelatin (75:25) treated with transglutaminase, which showed the lowest value of water vapor permeability (4.5 g.mm/m².d.KPa). The enzymatic intercrossing also prompted a substantial increase in the protein components of high molecular weight in the solutions used to make films.

Whey Proteins

This consists of different fractions such as β -lactoglobulin, α lactalbumin, bovine serum albumin and some immunoglobulins. β -lactoglobulin is the higher component (50-60%) of whey protein (Sothornvit and Krochta, 2000).

These proteins are very sensitive to high temperatures, i.e., the first to be denatured and to a lesser degree at acidic pH (contrary to that which happens with casein), due to their stability, which is by hydration and not by electrical charge. The films based on whey proteins are excellent barriers to O₂, but have been proven to be very fragile. As a solution to this problem, it was shown that mechanical properties were significantly improved through the addition of a plasticizer agent, such as glycerol. For the manufacture of films and coatings, this is part of a protein concentrate to which heat is applied to the denaturing. For example, Amin and Ustunol (2007) determined the effect of curing conditions at 90°C for 72 h, on the mechanical properties and the water solubility of the films based on whey protein (5% w/v) with glycerol (2.7 p/v). The heat treatment took place in the films at a force of the highest tensile strength (15.4 MPa) compared to in films without treatment (6.5 MPa). The moisture resistance of the cured films was greater than that of the films that were not cured (1.5 and 0.12 MPa, respectively). The water solubility of the films with whey protein decreased from 23.65 to 19.99% with curing time and a reduction of the plasticizer content.

Fang *et al.*, (2002) used whey protein isolated as the basis for edible films, by applying a heat treatment to cause its gelling. The effects of the proportions of whey protein, calcium, and glycerol (plasticizer) in the barrier properties and traction of the films were investigated. The films were developed with 12% whey protein dissolved in 5 or 10 mM calcium solution, and 20 or 40% glycerol. It was noted that by increasing the calcium concentration, the tensile strength was increased (17 to 21 MPa). In the same way, the increase in the elongation percentage was proportional to the percentage of glycerol added (29 to 95%). In general, the protein proportion had less of an influence on the tensile strength, elongation and permeability to water vapor in comparison with the glycerol concentrations and calcium ions. The microstructure analysis of the films revealed the influence of glycerol and calcium concentrations in the gel networks, which could be related to the traction properties of the films. The films prepared without calcium and with 5 mM calcium showed a uniform surface. The addition of 10 mM calcium caused an important protein aggregation, resulting in an uneven surface. With a glycerol content of 40%, the whey protein aggregates were most evident in the microstructure of films, forming spherical particles that were 50 nm in size. These particles abounded but were not as united to form a gel network, as well as in the case of the film with 20% glycerol.

Gelatin

Gelatin is a protein that is derived from collagen by alkaline or acidic hydrolysis. Collagen is the major constituent of the skin, tendons, and connective tissues and is widely distributed in the fibrous protein of animals. The benefits of this type of coating are to avoid the loss of moisture and provide a uniform appearance to the product by improving structural properties (Bigi *et al.*, 2002). In the formation of films, reducing the oxygen permeability, the diffusion of

water vapor and the migration of fats (Aguilar, 2005). The **films'** properties vary depending of the origin of gelatin; the amino acid composition of gelatins of different species is different, especially with regard to the major amino acids (Gly, Pro, Hyp) (Gomez *et al.*, 2011a). Thus, it has been recently seen that films based on tuna gelatin, which contain a low number of residues of Pro and Hyp, presented deformation values to break approximately 10 times greater than that obtained by the films based on gelatin of bovine hide (Gomez *et al.*, 2011b). Similarly, Avena *et al.* (2006) noted that the values of permeability to water vapor (0.93 g.mm/m².h.kPa) of the films based on cold-water fish gelatin were significantly lower than those of the films based on gelatin from temperate fish or mammals (1.31 and 1.88 g.mm/m².h.kPa, respectively) at 25°C and 80% relative humidity, with films that were 0.05 mm in thickness. This was related to the amino acid composition of the of cold-water fish gelatin (with a high content in hydrophobic amino acids and low level of Hyp). On the other hand, Castro and Gonzalez (2010) evaluated the physiochemical effect of the implementation of an edible coating formulated from two gelatin concentrations (4 and 8%), with the addition of 0.25% oregano oil as an antimicrobial agent on Cape gooseberry fruits (*Physalis peruviana*, L). The results showed that the coating was able to reduce the metabolic activity in the fruits coated with 36% with respect to the control fruits. The loss of weight decreased by 17.6%; the life of the berries increased by an average of 33%.

Proteins of the corn (zein) and wheat gluten

These are obtained by the drying of alcoholic dispersions used to solubilize proteins. These types of proteins form films with similar properties: bright, impervious to fat, with low levels of permeability to O₂ and CO₂ and low permeability to water vapor in comparison with other protein films (Ghanbarzadeh *et al.*, 2007).

Apricots of intermediate moisture were covered with different formulations of zein in edible films. The potential of antimicrobial and antioxidant agents in the edible film of zein and the effects of the coating to maintain apricots quality of intermediate moisture were investigated during 10 months of storage at low temperatures (5 and 20°C). The color change was significantly reduced by the coating process. The control fruits presented a higher ratio of a^*/b^* (1.0) than the coated fruits (0.7). The ΔE value of the coated samples was 7.9 at the end of the storage period, while that for the control samples was 13.8. The total count of viable bacteria in the control group was significantly higher than the samples coated with zein film. This film inhibited microbial growth to the extent of about 2 log between the control and the fruits covered. It was also found that at higher storage temperatures, the loss of moisture of the sample without film was higher than those at lower temperatures (Baysal *et al.*, 2010).

Other authors (Guo *et al.*, 2012) have investigated the effects of the zein proportion and wheat gluten (0/100, 20/80, 40/60, 60/40, 80/20 and 100/0 p/p), glycerol concentration (10, 20, 30 and 40 g/100 g), pH (12) and temperature of the heat treatment (40°C to 80°C) on the mechanical and barrier properties of the films. The results showed that the elongation of films increased from 10 to 78% when the glycerol concentration increased. On the other hand, the elongation first increased (55%) and then decreased (10%) when the ratio of zein/wheat gluten increased, along with heat treatment temperature and pH. The tensile strength of films rose from 5.0 to 6.0 MPa with elevation of the temperature of the heat treatment and the pH. The permeability to water vapor increased from 3.8 to 9.0×10^{-11} g/m.s.Pa, with the increase in the glycerol concentration, but decreased from 9.0 to 5.0×10^{-11} g/m.s.Pa, when the ratio of zein/wheat gluten, the heat treatment temperature and the pH of the solution increased in the formation of the films.

Multicomponent Mixtures

The objective of using mixtures between biopolymers for the development of edible films is to counteract the inherent shortcomings of each component and thus being able to complement and improve the properties and characteristics of the resulting material. An example of the formation of complex films is seen in the study of Denavi *et al.* (2009), who used increasing concentrations of soy protein isolated (0, 25, 50, 75 and 100%) and decreasing concentrations of cod gelatin in their respective complementary percentages. These authors noted that the formulation that contained 25% isolated soy protein and 75% cod skin gelatin showed an improvement of the

break force until 1.8 or 2.8 times greater than that obtained by the formulations with only gelatin or soy protein, respectively, while the relatively low permeability to water vapor (2×10^{-8} mm/h.cm².Pa) of the films of isolated soy remained. Also, it was found that the % of film deformation was decreasing when the proportion of cod gelatin was reduced. Another example is the study conducted by Muñoz *et al.* (2012), who produced edible films using a mixture of the chia mucilage and whey proteins in a proportion of 1:3 and 1:4 to pH 7 and 10, using glycerol as a plasticizer in a proportion of 2:1 mixture:plasticizer. The films produced at pH 10 and 1:3 ratio showed superior mechanical properties to the other films, with higher tensile strength (4.68 MPa) and elongation of 1732%. In addition, the films produced at pH 10 showed a better vapor barrier of water (0.62 g.mm/h.kPa.m²) than in the films at pH 7. The films with highest solubility (63.96%) were those developed with a proportion of 1:4 and pH 7. The use of this new polysaccharide was considered an option by which to modify and/or improve the physical properties of hydrophilic edible films.

Plasticizers agents for the formation of edible films

Plasticizers are compounds of low volatility that can be added to provide flexibility and elasticity to a polymer film. They are a very important factor in the formation of edible films since they affect the mechanical properties and permeability of the films. The plasticizers alter the structure of the films, the chain mobility and the diffusion coefficients of gases or water (Dutta *et al.*, 2009). In structural terms, plasticizers are inserted in the polymer matrix, by increasing the free space between the strings and resulting in a decline of intermolecular forces along polymer and therefore, gives it a greater molecular mobility, increasing its permeability to water, gases or aromas (Pérez and Baez, 2003). The intensity of these effects depends on the type, amount and molecular weight of the plasticizer agents.

The plasticizers that are used in the food industry include: Monosaccharides, disaccharides and oligosaccharides (glucose, glucose syrups and honey); polyols such as sorbitol, glycerol and polyethylene glycol and glycerol derivatives; lipids and derived (fatty acids, monoacyl glycerols, ester derivatives, phospholipids and surfactants (Parzanese, 2010).

Polyols are particularly effective as plasticizers, with glycerol being the most commonly used in the formulations of proteins films. On the other hand, sorbitol is a cryo protectant in addition to a plasticizer, and combination with glycerol increases the permeability to

water vapor and the mechanical resistance of the films; however, this slightly reduces the flexibility that produces glycerol. This fact, together with the fact that glycerol also produces a greater absorption of moisture than sorbitol, means that a combination of equal parts between both polyols is normally used to obtain this intermediate effect.

In a study (Bourtoom *et al.*, 2006) where edible films were made from fish proteins that are soluble in water, several types of plasticizers were tested: sorbitol, glycerol and polyethylene glycol. It was found that the type and concentration of the plasticizer significantly affects the mechanical and barrier properties of the films. The films laminated with sorbitol showed the highest tensile strength (3.14 MPa); however, its effect on the permeability to water vapor was low (30.41 g/mm.m².d.kPa). In contrast, laminating films with glycerol and polyethylene glycol resulted in a flexible structure in spite of having a low tensile strength (2.13 MPa and 1.80 MPa, respectively); these also presented greater permeability to water vapor (125.8 g/mm.m².d.kPa and 89.52 g/mm.m².d.kPa, respectively). As the concentration of sorbitol, glycerol and polyethylene glycol increased from 25 to 75% p/p, the tensile strength was reduced from 3.14 MPa to 0.82 MPa, from 2.13 MPa to 0.82 MPa and from 1.8 MPa 0.62 MPa, respectively, along with an increase in elongation at break (from 5.76 to 15%, from 26.24 to 61.01% and from 23.49 to 52.21%, respectively). The films laminated with glycerol generated the highest value of permeability to water vapor (230 g/mm.m².d.kPa), while those coated with sorbitol showed greater solubility (75%) in comparison with the other films. Also, a measure that will increase the plasticizer concentration, is film solubility; for example, those laminated with 25, 50 and 70% polyethylene glycol were 59, 65 and 70% soluble, respectively. The color of the films was more greatly affected by the nature of the plasticizer used than by its concentration. The use of glycerol and polyethylene glycol resulted in films with more yellow tones.

Kowalczyk *et al.*, (2014) tested the effects of glycerol (3 to 7% p/p), sorbitol (4 to 8% p/p), and pH (7, 9 and 11) on the formation of films with isolated pea protein. In general, laminating films with sorbitol exhibited significantly greater tensile strength, elasticity modulus as well as a minor break elongation compared with laminating films with glycerol. The incorporation of a greater proportion of glycerol and sorbitol in the films, resulted in decreases in the tensile strength (4 to 1.5 MPa for glycerol and 7 to 2 MPa for sorbitol), elasticity modulus (120 to 25 MPa for glycerol and 250 to 75 MPa for sorbitol), but did not affect the break elongation (for example, at pH 7, glycerol reported 80% and sorbitol reached 30%). The pH variation in film formation showed no effect on the elasticity

modulus; on the other hand, the pH had a great effect on film elongation. For example, the elongation percentage for the film made with 5% glycerol was 140% at pH 7, 110% at pH 9 and 80% at pH 11.

Characteristics of the edible films

The properties of edible films (permeability to water vapor and gases, solubility in water or lipids, water adsorption capacity, color, transparency, brightness, mechanical response, among others), depend on the type of material used, the conditions of film training, the plasticizer type, solvent nature, rate of solvent evaporation and its thickness, among others (Dick, 2014). To determine the purpose of the edible film, research is necessary. Below, some of the important characteristics to assess are briefly explained.

Physicochemical

Some of the physicochemical characteristics can be evaluated in films applied in the food industry, as defined below:

Solubility

This is an important factor in the development of films, since it determines its biodegradability when used as means to protect the food. Although it requires low film solubility during storage, high solubility might be advantageous during the cooking of products wrapped in film. The solubility of the films in water affects the use of film. For example, the films used on food with high moisture must be insoluble, while films used in the formation of pockets that will dissolve in water must be easily soluble. That is why it is necessary to determine the characteristics of the films in order to be able to subsequently find an application. Muller *et al.*, (2008) assessed the effects of concentrations of the sorbitol and glycerol plasticizers (0.25, 0.30 and 0.35 g/g dry starch) on the water vapor permeability and the solubility of films made with cassava starch to 3% p/v. The trials were carried out in three ranges of relative humidity (2-33%, 33-64% and 64-90%). These authors observed a strong influence of the plasticizer concentration on the barrier properties of films; that is to say, the permeability to water vapor increases by increasing the plasticizer concentration. For example, the films developed with 0.25 and 0.35 g of -7 glycerol obtained a permeability of 1.59 x 10⁻⁷ and 2.42 x 10⁻⁷ g/m².Pa.h, respectively. It was concluded that because of the hydroxyl groups of plasticizers, the films became more hygroscopic, thus

increasing solubility. In this sense, the solubility of the films laminated with 0.25 g of sorbitol was 7.40×10^{-6} , increasing to 8.94×10^{-6} in the presence of 0.35 g of the plasticizer concentration.

Surface Appearance by scanning electron microscopy (SEM)

To analyze homogeneity and the surface appearance of edible films, as well as the intercrossing of raw materials used, scanning electron microscopy (SEM) can be used. The resolution of the microscope is such that it allows the study of characteristics of the materials at a very small scale. Acosta *et al.*, (2013) studied the film formation of cassava starch added with gelatin in proportions of 0:100, 50:50, 75:25 and 100:0, respectively, and fatty acids esters to 15% p/p with respect to the polymer. Glycerol was used as a plasticizer in a ratio of 1:0.25 polymer:glycerol and evaluated the effect on mechanical and barrier properties, stored for 5 weeks. The micro structural analysis of the films was studied through the use of SEM. It was noted that the addition of gelatin in the film formulation of cassava starch improved mechanical properties (elastic modulus = 131 MPa in films without gelatin and 627 MPa in films with 50% gelatin). The incorporation of fatty acid esters reduced the permeability to water vapor; for example, the starch film made with 50% p/v of gelatin decreased the permeability from 5.2 to 3.8 g.mm/KPa.h.m² when the lipid material was incorporated. The micrographs showed a compact structure in the pure films, while the composite films presented a more heterogeneous surface but with good compatibility between starch and gelatin. Also, the formation of lipid aggregates was observed across the entire array of the film.

Identification of the functional groups by the Fourier transforms infrared radiation (FTIR)

This technique is based on the absorption of infrared radiation (IR) by molecules in vibration. A molecule will absorb the energy of a beam of infrared light when the incident energy is equal to that required to produce vibrational transition of the molecule; that is to say, the molecule starts to vibrate in a certain way because of the energy supplied to it. Two basic categories of vibrations can be distinguished: tensile and flexing strength. The vibrations of tensile strength involve changes in the interatomic distance along the axis of the link between two atoms, while the bending vibrations are caused by changes in the angle formed by two links. Each molecule presents a characteristic IR spectrum (fingerprint),

because all of the molecules have some vibrations which, when activated, cause the absorption of a specific wavelength in the area of the electromagnetic spectrum corresponding to infrared. In this way, determining the wavelength that absorbs a substance in this area of the spectrum can enable the identification of information about those molecules that make up the substance (Lopez, 2011). An example of the application of this technique is a study where chitosan films were prepared using 2% w/v with different bioactive compounds based on proteins (a fraction of peptides from concentrated whey protein hydrolysate, glycomacropeptide and lactoferrin) and glycerol to 1% p/v as a plasticizer. FTIR analyses were used to evaluate the possible chemical interactions between the polymer film and the bioactive agents embedded in it. Different intensities of chemical interactions were found between chitosan and proteins, which were represented by bands of amide I (between 1600 and 1700 cm⁻¹), amide II (around 1536 cm⁻¹), and NH and CO deformations (1580-1490 and 1700-1630 range cm⁻¹, respectively) (Bourbon *et al.*, 2011).

Weight variation with respect to the temperature by thermogravimetric analysis (TGA)

This analysis determines changes in the weight of the film with the increase in temperature. The TGA allows determination of the resistance of the packing material with the knowledge of the variation in material weight (loss or gain) as a function of time, while the sample is subjected to a controlled increase in temperature. This determination of the films defines the temperature conditions at which the material begins to decompose (Espitia *et al.*, 2014). Sanchez *et al.*, (2015) developed and characterized biodegradable films based on extracts of pectic bagasse of Mexican lemon, incorporated with glycerol and lemon essential oil. Mechanical and permeability tests were performed to water vapor, to select a formulation with greater resistance and lower permeability. The film selected on the basis of pectic bagasse of lemon extract (1.0% pectin, 0.75% glycerol, 500 mg/kg lemon essential oil) was characterized in terms of FTIR, TGA, and SEM. The weight loss curves were obtained and derived from the loss of weight/°C as a function of the increase in temperature. These curves showed five weight loss areas. The first zone is found below 60°C with a weight loss of nearly 10%; this was due to a loss of moisture as well as to the evaporation of the essential oil added to the film due to the high volatility of the compounds present in essential oils. The weight loss that was from 100 to 163.92°C (second zone) was due to the moisture loss in the sample; this could include water,

glycerol or other alcohols present (for example, hydroxyl groups from sugars and polyphenols). The third and fourth area resulted from the degradation of short and long-chain pectins. The fifth peak was associated with branched chains of polymers. The sum of these losses accounted for 8.3% of the weight of the total sample. The residual weight of the film sample analyzed was 19.8%.

Thermal behavior by differential scanning calorimetry (DSC)

The determination of the glass transition temperature (T_g) is extremely useful for predicting the behavior of the materials as it governs the mechanical properties of amorphous polymers, controls the crystallization kinetics of these materials and the diffusive processes that occur in them. It is usually determined by DSC and may employ the technique of Dynamic Mechanical Analysis (DMA) to determine the relaxation temperatures associated to the glass transition. In addition this technique allows changes in the microstructure of the films and their viscoelastic properties to be studied (Chen *et al.*, 2007). From different proportions of cassava starch and protein isolated from soy, Saavedra and Algecira (2010) developed different types of films while maintaining the composition of 2 g of material hydrocolloid (starch and protein), 2 g glycerol and 0.4 g of oil per 100 g of solution. These films were characterized through mechanical and thermal testing. For the thermal analysis, DSC, with a ramp from -60°C to 150°C at a heating rate of $5^\circ\text{C}/\text{min}$ with a modulation of $1^\circ\text{C}/\text{minute}$ in inert atmosphere with N_2 injection, was used. The thermograms obtained showed whether there was an interaction between starch and protein, which is manifested in the increase of the thermal transition temperature for the mixture compared with the pure components (from 105 to 115°C , approximately) and with the decrease in the heat flow needed to carry out the process with these two hydrocolloids (80 mW for hydrocolloids separately and 70 mW when they are mixed).

Degree of crystallinity in the sample by X-ray Diffraction

This technique allows information about the structure of the analyzed material to be obtained since the diffraction diagram is like a "fingerprint" of the crystalline substances. The determination of the proportion of solid that is crystalline (its crystallinity) often have considerable practical importance, since growing crystallinity has the useful effect of improving properties such as resistance and rigidity; resistance to the dissolution and dimensional stability (thermal softening). A spectrum of X-ray

diffraction of a semi-crystalline material is characterized by the presence of absorption peaks and a zone of amorphous contribution; the greater this area, the lower the degree of crystallinity in the sample is. The work performed by Lopez (2011) was dedicated to the development of films based on starches (maize, cassava and ahipa) and chemically modified corn starches. The XRD patterns were evaluated and the crystallinity degrees of the starches. The corn starch granules presented a diffraction pattern type A typical of cereals; however, the peaks that are located in $2\theta = 15, 18$ and 23° registered the higher intensity. The allocation of the pattern for the case of the ahipa and cassava was not easy. The XRD patterns presented peaks at $2\theta = 5.5, 15.4, 17.0, 18.0, 20.0$ and 23.5° , which were assigned a Type C pattern (Geng *et al.*, 2007). This pattern is typical of legume starches and of tropical fruit and tuber starches. It was noted that the botanical origin of the starch affected the degree of crystallinity of the granules; this variation might relate in reverse order with the amylose content.

Ability to wetting by the contact angle

The measurement of contact angle, which refers to the angle formed between the water drop deposited and the film, can be interpreted as the degree of hydrophobicity and wetting capacity of the contact material. This reflects both the total distribution in liquid until null adhesion; a high contact angle reflects hydrophobicity and one under reflects the water affinity (Porrás *et al.*, 2015). Usually, the films with high values of contact angle exhibit a high concentration of hydrophobic groups on the surface, which increases its barrier properties against moisture and reduces its wetting. Porrás *et al.*, (2015) developed films composed of protein isolated from whey and mesquite gum to 10% p/p in the following proportions (%) of protein-gum: 91-9, 93-7, 95-5, 97-3, 99-1; here, 30% sorbitol (p/p with respect to the hydrocolloids) was used as a plasticizer. The effect of heat treatment in the wetting properties was evaluated by means of the contact angle formed between a water drop and one of the faces of the film surface; also, the thermal transitions were analyzed by DSC and the protein-polysaccharide interactions by FTIR. The results indicated that the thermal denaturation reduced the wetting properties, for example, in the film formed with protein-gum 95-5%, the contact angle at 20°C was 43.1° and when raising the temperature to 90°C , the angle increased to 59.3° (the film decreased its wetting). Also, the increase in the proportion of mesquite gum in the films, restricted wetting properties; in this case, the film formed with protein-gum 99-1% obtained a contact angle value of 42.6° , increasing up to

45.0° in the films formed with protein-gum 91-9%. In conclusion, there was a difference in the dampening effect of the heat treatment of the solutions, that is to say, the heat exposure decreased the wetting of the film.

Mechanical

The tensile strength, elongation and modulus of elasticity are all mechanical properties of the edible films that can be used to describe the behavior of the material. The tensile strength or hardness is the maximum force per area that a film can withstand before breaking; this is obtained by dividing the maximum force between the cross-sectional area of the film. The elongation is the percentage of maximum change in the length of the film before breaking, and at a lower elongation percentage, less flexibility. The modulus of elasticity indicates the relationship between tensile and strain in a solid body (Wang *et al.*, 2007). In various studies, it has been observed that increasing the value of the tensile strength, the percentage of elongation decreases and vice versa (Peressini *et al.*, 2004; Brindle and Krotcha, 2008). A study by Wang *et al.* (2007) assessed the capabilities of training film with six types of proteins, as well as six types of polysaccharides at several concentrations (proteins: 0-16%, polysaccharides: 0-4%), heating temperatures of 60 to 80°C and glycerol as a plasticizer (50% p/p). Biopolymers evaluated in the films included the following proteins: sodium caseinate (SC), whey protein isolate (WPI), and gelatin (G) and the polysaccharides: carboxymethyl cellulose (CMC), sodium alginate (SA) and potato starch (PS). The films produced on the basis of 1.5% SA, 8% G, and 3% of CMC had the higher tensile strength (24.8 MPa), greater tear resistance (0.30 N) and greater resistance to perforation (22.6N), respectively. In general, the films made with polysaccharides presented higher tensile strength values in comparison with the films made with proteins. However, the films with polysaccharides experienced lower percentage values to elongation. For example, the films of gelatin to the 8% presented a tensile strength of 6.6 MPa and an elongation percentage of 89.6%, while values of 11.2 MPa for tensile strength and 10.5% for elongation were obtained with films made with 2% carboxymethyl cellulose.

Barrier

Another important property of the films is its function as a barrier against moisture, if you are looking for edible films that diminish the transfer of moisture between the product and the environment. This property is measured with the value of permeability to water and it is required to be as

low as possible (Qiu and Wen, 2008). The chemical structure, relative polarity, degree of crystallinity, density, molecular orientation, degree of cross-connections between molecules, molecular weight and polymerization and the presence of plasticizers and additives, directly influence the barrier properties of water vapor of the edible films (Wu *et al.*, 2002). The gas permeability, in particular to O₂ and CO₂, is another factor to take into account that already can greatly influence the stability of the food that is sensitive to the oxidation of lipids, vitamins and pigments, in the life of the coated product, if you limit the availability of such gases. The measurement of the permeability to O₂ can be made using an O₂ analyzer, while the CO₂ or any other gas can only be done through a gas chromatograph (Pastor, 2010).

Prommakool *et al.*, (2010) used whey protein isolate (WPI) combined or not with a polysaccharide obtained from the okra fruit (OKP) to make films using edible glycerol (Gly) as a plasticizer. The proportions of these materials (WPI:OKP:Gly) that were evaluated were the following: 75:0:25, 56:19:25, 37.5:37.5:25, 19:56:25 and 0:75:25. The mechanical and barrier properties of the films were analyzed. The films developed only with WPI and glycerol (75:0:25) showed the permeability to lower water vapor (PVA = 2.6 mm.g/m².h.kPa), while those formed only with OKP and glycerol (0:75:25) obtained the highest values (PVA = 4.3 mm.g/m².h.kPa). The combination of OKP with WPI to make films resulted in a significant increase in PVA in comparison with the film prepared only with WPI. For example, the film with a relationship of 37.5:37.5:25 obtained a PVA = 3.8 mm.g/m².h.kPa. The values for permeability to oxygen (PO) increased, to raise the proportion of OKP in films. In this sense, the film made only with WPI obtained a PO = 46.4cm³.µm/m².d.kPa, while those with WPI:OKP:Gly of 9:56:25 showed a PO = 139.5 cm³.µm/m².d.kPa. In general, to increase the ratio of protein in the film, the passage of oxygen was restricted to a greater extent.

Optics

The appearance or aspect is another of the quality factors that is critical to the acceptance of a product to the consumer. The optical properties of the films are related to its opacity (transparency), color and brightness. The color can be considered an important parameter in the characterization of the films, since it is related to the raw material used in the elaboration of the same. For example, Tapia *et al.*, (2005) made films with 4% amaranth flour and laminated with 22% glycerol at pH 10. They evaluated

the mechanical properties and optical barrier in the films. The color analyses registered values of L, a, b = 89.97, -1.16, 8.09 and $\Delta E = 8.89$, which means that slight yellowing with moderate opacity (6.45) was evident. In another study, Cao *et al.*, (2007) developed films on the basis of isolated soy protein (SPI) at 10% p/p and glycerol at 0.1 g/g protein, which were then added to gelatin (G) in the following proportions = SPI:G, 10:0, 8:2, 6:4, 4:6, 2:8, 0:10. In the films formed, the opacity was measured by means of a spectrophotometer at 500 nm. It was noted that a large proportion of gelatin (SPI:G, 2:8) led to a film that was less opaque (2.63), as a result of the presence of a lower amount of insoluble particles.

CONCLUSION

At the global level, it is estimated that 25 million tons of plastic materials from non-renewable sources such as petroleum, accumulate in the atmosphere each year and can remain unchanged for a period between 100 and 500 years. These materials are not biodegradable and result that several thousands of tons of them are deposited in dumps, increasing each year the problem of municipal waste disposal. The use of biopolymers for the development of new biodegradable materials in the food industry, constitute an alternative to reduce the production of the materials coming from petroleum. In addition, it can achieve benefits for the environment by reducing pollution and economic benefits in the production of raw materials, since many of these materials could be obtained from by-products as chia mucilage. Thus, this review documented the chia potential as resource for edible films development as well as some variables that influence the formation of films and the most important features by which to evaluate them in order to define the application in the food industry.

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