BIOPOLYMERS USED IN FOOD PACKAGING: A REVIEW

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Abstract: The aim of this review is to reveal the most relevant biopolymers mentioned in the literature, which are used and have great potential applications in food packaging. Most works that we have investigated classified the biopolymers ranked in three categories namely: biopolymers from renewable sources, chemically synthesized biopolymers and microbial synthesized biopolymers. In this work, the biopolymers are classified according to their general chemical composition.

Keywords: biopolymers, food packaging, polysaccharides, proteins, aliphatic polyesters

INTRODUCTION

The actual tendency in packaging research is to develop and promote the use of “bio-plastics” which are useful in reducing waste disposal and are good replaces of petroleum, a nonrenewable resource with diminishing quantities (Ruban, 2009) (Souza et al., 2010).

The problems in disposing of the huge quantities of waste generated by non-biodegradable food packaging have led to the study of biopolymers as materials to be used as edible coatings in food packaging (Azeredo et al., 2012).

Development of materials from natural polymers for different applications has been a hot topic for several years due to increasing prices of petrochemicals and increasing environmental concerns (Farris et al., 2009) (Laine et al., 2012). For more natural products, bio-based films or biopolymers, improving the quality of many products is important to satisfy

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the consumers demanding of more environmentally friendly packaging. This approach will continue to play an important role in the food industry (Cutter, 2006), (Satyanarayana et al., 2009).

Today the use of polymers from renewable sources in food packaging is growing (Mensitieri et al., 2011). To enlarge the shelf-life of all types of foods with increasing the preservation and protection from oxidation and microbial spoilage the tendency is to use more natural compounds. The use of synthetic films has led to big ecological problems because this materials are non-biodegradable (Sabiha-Hanim and Siti-Norsafurah, 2012).

The natural biopolymers that are used in food packaging have the advantages to be available from replenishable resources, biocompatible, biodegradable, and all this characteristics led to ecological safety (Prashanth and Tharanathan, 2007). The structure of monomer used in polymer preparation is directly effective on the properties that are required in different areas of work, such as: thermal stability, flexibility, good barrier to gases, good barrier to water, resistance to chemicals, biocompatibility, biodegradability (Güner et al., 2006).

(Mensitieri et al., 2011) says that polymers extracted or removed from natural resources can be degraded and transformed under different environmental conditions and under the action of different microorganisms. Some authors classified the polymers according to the method of production or their source as:

A: Polymers directly extracted or removed from vegetal or animal biomass such as polysaccharides and proteins;

B: Polymers produced by classical chemical synthesis starting from renewable bio-based monomers such as polylactic acid (PLA);

C: Polymers produced by microorganisms such as polyhydroxyalkanoates, cellulose, xanthan, pullulan (Ruban, 2009) (Nampoothiri et al., 2010) (Mensitieri et al., 2011).

Polysaccharides such as starch, and cellulose, are natural polymers, called biopolymers, wich are found in nature during the growth cycles of all organisms. Other natural polymers are the proteins which can be used to produce biodegradable materials. This polymers are often chemically modified whit the goal to modify the degradation rate and to improve the mechanical properties (Vroman and Tighzert, 2009). Figure 1 presents schematically a classification of biopolymers according to the general chemical composition.

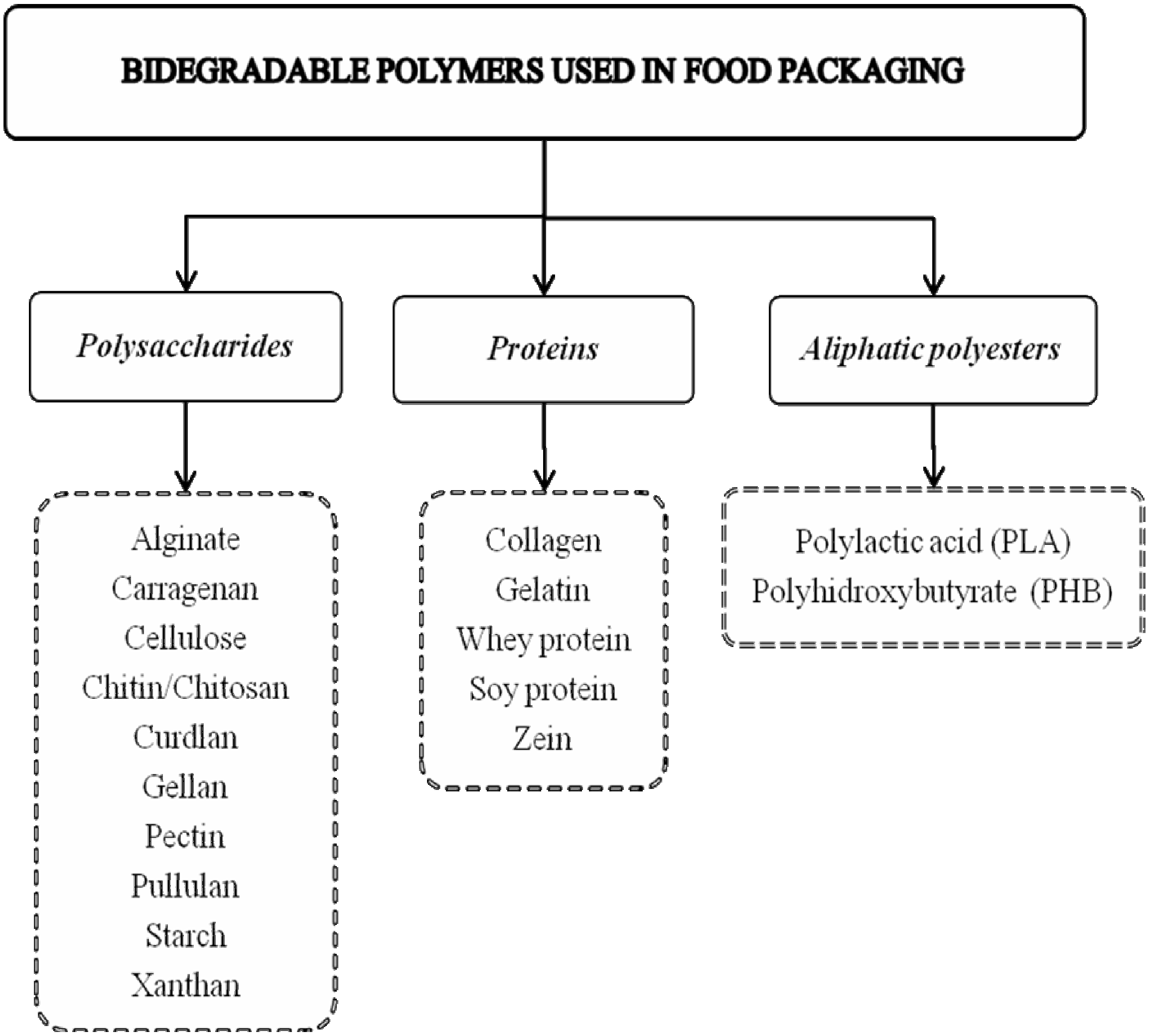

Figure 1. Clasification of biopolymers depending on the general chemical composition

Biopolymer-based packaging materials originated from naturally renewable resources such as polysaccharides, proteins, and lipids or combinations of those components have the potential to replace current synthetic plastics (Sothornvit, 2009) (Aloui et al., 2011). At this moment, bioplastics cover approximately 5–10% of the current plastic market (Vieira et al., 2011).

POLYSACCHARIDES

- **Alginate**

Alginate is another polysaccharide, extracted from brown algae such as *Laminaria* and *Macrocystis* (Tapia et al., 2008) (De Lima et al., 2009). Alginate is a binary copolymer and it contains carboxyl groups in each constituent residue. Its structure is composed of β-D-mannuronic acid monomer linked to α-L-guluronic acid monomer, through α 1,4-glycoside linkage (George and Abraham, 2006). The ratio between the two monomers varies with the sources (Augst et al., 2006).

Bacterial alginate was extracted from *Azotobacter vinelandii* (Moresi et al., 2004).

Alginate has been used in the past in food industries as thickening agent, gelling agent and colloidal stabilizer (Sriamornsak and Kennedy, 2008).

- **Carrageenan**

Carrageenan is derived from red seaweed (*Kappaphycus alvarezii*, formerly *Eucheuma cottonii*) (Chan et al., 2013) and has good gas barrier properties (Hamzah et al., 2013). Carrageenans are anionic linear sulphated polysaccharides composed of D-galactopyranose residues bonded by regularly alternating α-(1 /3) and β-(1 /4) bonds, (Karbowiak et al., 2008), (Martins et al., 2012).

Carrageenan is one of the three dominant carrageenan species, i.e. κ, ι, and λ-carrageenan, which differ in their disaccharide structures. κ-carrageenan is mainly used in food applications (Kong and Ziegler, 2013).

In the food industry, k-carrageenan is used as a gelling, thickening, stabilising, and water-binding agent in various food products (Chan et al., 2013).

- **Cellulose**

Cellulose is one of the most abundant biopolymers in the nature and acts as a reinforcement material in plants and bacteria (Pandey et al., 2012). Cellulose molecules has amphiphilic character and has a high density of hydroxyl groups (Rein et al., 2012), and consists of a chain of β-(1→4)-linked glucose residues.

In recent years cellulose has been extracted from green algae (*Valonia, Halicystis, Cladophora)*, from the brown alga *Laminaria* and from others (Siddhanta et al., 2009). This type of cellulose has unique and special structural and mechanical properties and high hydrophilic nature (Fu et al., 2013).

Some bacteria belonging to the genera *Gluconacetobacter*, *Sarcina* or *Agrobacterium* are able to produce a particular type of cellulose, designated as bacterial cellulose (Carreira et al., 2011).

- **Chitin/Chitosan**

Chitin is the universal and characteristic component of all the fungal groups. *Aspergillus niger* contains only chitin (Muzzarelli et al., 2012).

Chitosan is a aminopolysaccharide (Pillai et al., 2009) (Sergeev et al., 2012) a de-N-acetylated derivative from chitin (Fernandez-Saiz et al., 2010). Chitosan is a hydrophilic hetero-polysaccharide (Fajardo et al., 2010) consisting of linear β–1,4-linked GlcN and GlcNAc units (Prashanth and Tharanathan, 2007). Chitosan can be obtained from wastes obtained in the shellfish industry, and from this reasons is an abundant material that is currently offered. It can be obtained from the chitin component of fungal cell walls (*Aspergillus fumigates, Histoplasma farciminosum*) and from the yeast *Saccharomyces cerevisiae,* too (Fernandez-Saiz et al., 2010) (Merzendorfer, 2011).

The forms of *Mucor rouxii (*filamentous and yeast-like) contains large quantities of chitosan (Muzzarelli et al., 2012).

Chitosan loses its positive charge at higher pH values (> 6.5) and becomes insoluble in aqueous solutions, which limits its application in food or pharmaceutical products at neutral pH (Li et al., 2010). Nevertheless, chitosan has multiple applications in food and nutrition because its high nutritional quality (Talens et al., 2012). Chitosan is used in different areas such as biotechnology, material science, and others fields (Di Pierro et al., 2011). Chitosan has strong antimicrobial properties against fungi, bacteria and viruses, its biocide properties being known for many years (Fernandez-Saiz et al., 2008) (Di Pierro et al., 2011).

- **Curdlan**

Curdlan is a water-insoluble bacterial glucan polysaccharide produced by *Alcaligenes faecalis* var. *myxogenes* and *Agrobacterium sp*. and is composed of a linear homopolymer of D-glucose with β-1, 3 linkages. Curdlan has heat-gelling and water-binding functionalities very important to the food industry (Funami and Nishinari, 2007) (Wu et al., 2012).

- **Gellan**

Gellan is secreted and extracted from the bacterium *Sphingomonas elodea* (previously named *Pseudomonas elodea*) (Rojas-Graü et al., 2008).
Gellan gum is a linear anionic hetero polysaccharide having a tetrasaccharide repeating unit consisting of rhamnose, D-glucose and D-glucoronic acid in the ratio of 1:2:1. It has the potential for partial or total replacement of existing gelling agents (Chaudhary et al., 2013).

- **Pectin**

From sugar extraction results a lot of residues, the most relevant is represented by sugar-beet pulp, which is a rich source of pectin (Mesbahi et al., 2005).
Pectin is an anionic biopolymer soluble in water and it is one of the major structural polysaccharides of higher plant cells and consists on chains of linear regions of (1→4)-α–D-galacturonosyl units and their methyl esters, interrupted in places by (1→2)-α–L-rhamno- pyranosyl units (Medeiros et al., 2012).
The applications of pectin in different industries (food and beverage) were as thickening and gelling agent, and colloidal stabilizer, texturizer, emulsifier (Mesbahi et al., 2005) (Sriamornsak and Kennedy, 2008).

- **Pullulan**

Pullulan is a non-ionic polysaccharide produced extracellular by the fungus *Aureobasidium pullulans*. It consists of a succession of maltotriose type units i.e. α-(1→6)-linked (1→4)-α-D- triglucosides. Pullulan is readily soluble in water but insoluble in organic non water-miscible solvents (Dias et al., 2011).
In present pullulan is used for different applications in medicine, food, cosmetics and ecology, with various purposes, such as: blood plasma substitutes, additives, flocculants, resins, and remediation agents (Cheng et al., 2011).

- **Starch**

Starch is a well–known hydrocolloid biopolymer and is produced by agricultural plants in the form of granules of various sizes within the endosperm, which are hydrophilic. The most important sources of starch extraction are potatoes, corn, wheat and rice. It is composed of 30% amylose (poly-α-1,4-D-glucopyranoside), a crystalline polymer and 70%

amylopectine (poly-α-1,4-D- glucopyranoside and α-1,6-D-glucopyranoside) and less than 1% proteins and lipids, a branched and amorphous polymer (Fredriksson et al., 1998) (Ratnayake et al., 2001) (Svihus et al., 2005) (Castillejo et al., 2012).

Starch is a great to enforce the textural properties of many foods and is widely used in food and industrial applications as a thickener, colloidal stabilizer, gelling agent, bulking agent and water retention agent (Singh et al., 2007).

- **Xanthan**

Xanthan gum, is an polysaccharide synthesized by aerobic fermentation of the bacterium *Xanthomonas campestris* (Laneuville et al., 2012).

Xanthan consists of 1,4-linked β-D-glucose residues having a trisaccharide side chain attached to O-3 of alternate d-glucosyl residues. The side chains are (3 → 1)-α-linked d-mannopyranose, (4 → 1)-β-D- mannopyranose and (2 → 1)-β-D-glucuronic acid, which account for the anionic properties of xanthan gum (Heyman et al., 2012).

Xanthan gum is largely the most important commercial microbial hydrocolloid used in the food industry as a thickening agent and stabilizer (Flores et al., 2010).

PROTEINS

- **Collagen**

Collagen is the primary protein component of animal connective tissues. In this tissue there are many types of collagen (over twenty types). Collagen is composed of different polypeptides, which contain mostly glycine, proline, hydroxyproline and lysine. Some differences in amino acid composition are apparent across collagens derived from different sources. There are certain features that are common to and uniquely characteristic of all collagens (Karim and Bhat, 2009) (Vroman and Tighzert, 2009).

- **Gelatin**

Gelatin is a protein obtained by hydrolyzing the collagen contained in bones and skin (Gómez-Guillén et al., 2009). Gelatin obtained from mammalian sources (porcine and bovine), is the most important and most used (Karim and Bhat, 2009). His structure is determined by the properties of collagen from which gelatin is obtained (Staroszczyk et al., 2012).

In the last years, in the food industry, the number of new applications for gelatine has increased. The new applications found for gelatin in food products are very diverse, from emulsifiers and foaming agents to stabilizers, and biodegradable films. All this applications are given by the growing demand to replace synthetic agents with natural and biodegradable ones (Gómez-Guillén et al., 2011).

- **Soy protein**

Soy protein has been used since the 19th in a variety of foods. The main characteristics of soy proteins that are useful in food industry are emulsification and texturizing (Vroman and Tighzert, 2009).
Soy protein exists as soy flour (SF) which requires less purification, soy protein isolate (SPI) and soy protein concentrate (SPC). Chemically, SPI contains 90% proteins and 4% carbohydrates, SPC contains 70% proteins and 18% carbohydrates, SF contains about 52% proteins and 32% carbohydrates. SF is the least expensive variety of these three forms (Giancone et al., 2009).
Soy protein can be used in the manufacture of adhesives, plastics, and packaging materials and can be a good alternative to the petroleum polymers (Tian et al., 2011).

- **Whey protein**

Whey proteins are a by-product from the cheese industry, and consist of whey protein isolates (WPI) witch represent the purer form of such proteins. Another form of whey proteins are whey protein concentrate (WPC) (Ramos et al., 2012).
Whey proteins are capable to form elastic films (Wang et al., 2013), and they have been employed as raw material for biodegradable packaging because they have good oxygen barrier and moderate moisture permeability (Ramos et al., 2012) (Popović et al., 2012).

- **Zein**

Zein, is the major storage protein of corn (*Zea mays L.*) and is a naturally occurring protein polymer obtained as a product of industrial corn processing that has been used to develop various types of thermoplastic products (Biswas et al., 2006) (Del Nobile et al., 2008) (Reddy and Yang, 2011).
The high content of non-polar amino acids gives corn zein a relatively hydrophobic nature and this feature lead to obtaining excellent barrier to

oxygen but instead lead to poor mechanical properties (Ozcalik and Tihminlioglu, 2013).

ALIPHATIC POLYESTERS

- **Polilactic acid (PLA)**

Poly (lactic acid) PLA, a biodegradable polymers (aliphatic polyester) is obtained from agricultural products such as corn, sugarcane, and others sources. (Satyanarayana et al., 2009) (Bang and Kim, 2012).
In the process of the fermentation of sugars various monomers are produced, that are converted to polymers (Okada, 2002). PLA is synthesized from lactic acid produced via starch fermentation from lactic bacteria. Starch is converted into sugar and after that the sugar is fermented to give lactic acid. The lactic acid prepared by this biotechnological method is almost exclusively L-lactic acid (Wee et al., 2006). PLA can be found as a polymeric helix and can exist in 3 stereochemical forms: poly (L-lactide) (PLLA), poly (D-lactide) (PDLA), and poly (DL-lactide) (PDLLA), with extremely various tensile properties, depending on what its degree of crystallinity is (Garlotta, 2002) (Madhavan Nampoothiri et al., 2010).
PLA is a hard material and its hardness is similar to acrylic plastic, is not soluble in water and it is completely degraded under compost conditions; but exists microorganisms, in marine environments, that can degrade it. PLA can achieve excellent mechanical properties (Vroman and Tighzert, 2009) (Bang and Kim, 2012).
PLA polymers are materials that are creating a lot of interest in the packaging industry for its properties and earth-friendly biodegradability. His properties are: resistance to oil-based products, seal ability at lower temperatures, and can act as flavor or odor barriers for foodstuffs (Ruban, 2009).

- **Polyhidroxybutyrate (PHB)**

Poly(3-hydroxybutyrate) (PHB) is one of the biodegradable PHA (polyhydroxyalkaoates) and is a naturally occurring β−hydroxyacid (a linear polyester) (Trainer and Charles, 2006) (Sanchez-Garcia et al., 2010) (Vieira et al., 2011). The general structure of the repeating units of these polyesters is different depending on the type of bacteria and the feed, it is typically -$(CH_2)_n$-CH_3 for most naturally occurring PHAs (Yalcin et al., 2006)

There are many microorganisms which accumulate PHB, but the most widely studied bacterium is *Ralstonia eutropha*, due to its ability to accumulate large quantities of PHB (Khanna and Srivastava, 2005)

Another microorganisms that accumulates PHB are: *Haloferax mediterranei, Halomonas boliviensis*, *Bacillus megaterium* and others (Quillaguamán et al., 2006) (Tan et al., 2011) (Liu et al., 2011).

Poly-[(R)-3-hydroxybutyrate] (PHB) is a linear, isotactic, semicrystalline biopolymer based on (R)-3-hydroxybutyric acid and has relatively high glass transition and melting temperatures. This aren't good features for packaging applications. With the purpose to improve flexibility, PHB is synthesized with various co-polymers such as poly-(3-hydroxyvalerate) (HV) leading to a decrease of the glass transitions and melting temperatures (Špitalský et al., 2006) (Modi et al., 2011).

Current applications of PHB-based polymers or composites include the packaging industry, medicine, pharmacy, agriculture, food industry (Valappil et al., 2007).

CONCLUSIONS

This review covers the major concerns about the natural polymers, their structure, sources and uses.

The most interesting and relevant biopolymers are analyzed, encompassing the whole range of polymers that have applications in food packaging.

Biopolymers have vast diversity, and therefore their applications in food packaging are various and multiple.

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