Chapter 8

BIOPOLYMERS FOR FOOD PACKAGING

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INTRODUCTION

Biopolymers are polymers that are generated from renewable natural sources, are often biodegradable, and not toxic to produce. They can be produced by biological systems (*i.e.* micro-organisms, plants and animals), or chemically synthesized from biological starting materials (e.g. sugars, starch, natural fats or oils, *etc*.).Biopolymers are an alternative to petroleum-based polymers (traditional plastics).The bio molecules in our body include proteins and peptides, DNA, and RNA.

CLASSIFICATION OF BIOPOLYMERS

Biobased polymers may be divided into three main categories based on their origin and production.

1) Polymers directly extracted/removed from biomass. Examples are polysaccharides such as starch and cellulose and proteins like casein and gluten.

2) Polymers produced by classical chemical synthesis using renewable biobased monomers. A good example is polylactic acid, a biopolyester polymerized from lactic acid monomers. The monomers themselves may be produced via fermentation of carbohydrate feedstock.

3) Polymers produced by microorganisms or genetically modified bacteria. To date, this group of bio based polymers consists mainly of the polyhydroxyalkonoates, but developments with bacterial cellulose are in progress.

COMMON BIO POLYMERS USED FOR FOOD PACKAGING

1. Polysaccharides

(i) Pectin: 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 .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.It is a structural hetero polysaccharide found in the primary cell walls of terrestrial plants such as sugar beet. The biopolymer films of pectin were totally grease proof and also showed improved barrier properties against oxygen and water vapour.The applications of pectin in different industries (food and beverage) were as thickening and gelling agent, and colloidal stabilizer, texturizer, emulsifier.

(ii) Chitosan/Chitin: Chitosan, the β-1-4-linked polymer of 2-amino2-deoxy-β-d-glucose, is prepared by the N-deacetylation of chitin, the second most abundant natural biopolymer after cellulose. Chitosan is soluble in dilute aqueous acid solutions and has been widely studied

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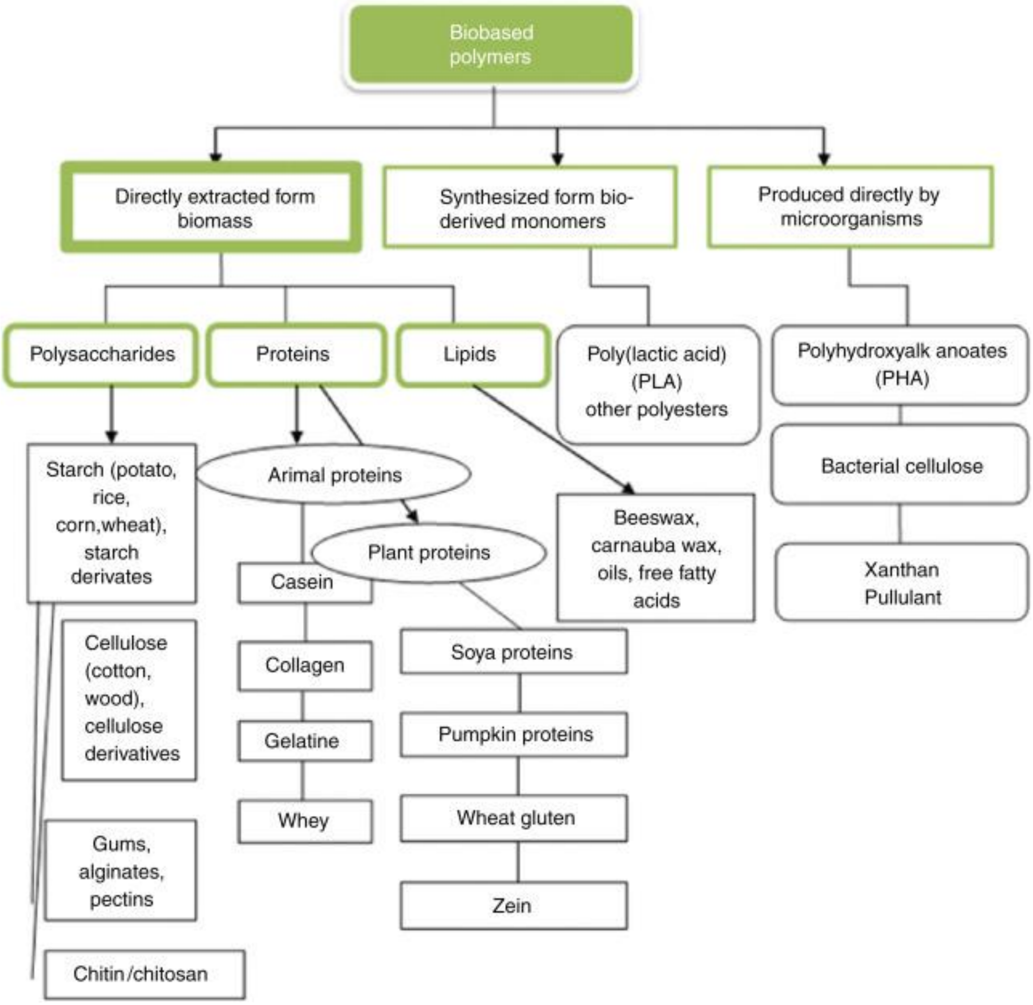
due to its good film forming properties. Chitosan can be used as such in cast free standing films or it can be applied as a coating onto paper/board or plastic films.



(iii) Alginate: Alginate is another polysaccharide, extracted from brown algae such as Laminaria and Macrocystis. 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. Bacterial alginate was extracted from Azotobacter vinelandii. Alginate has been used in the past in food industries as thickening agent, gelling agent and colloidal stabilizer.

(iv) Carrageenan: Carrageenan is derived from red seaweed and has good gas barrier properties. Carrageenans are anionic linear sulphated polysaccharides composed of D-galactopyranose residues bonded by regularly alternating α-(1 /3) and β-(1 /4) bonds. 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. In the food industry, k-carrageenan is used as a gelling, thickening, stabilising, and water-binding agent in various food products.

(v) Cellulose: Cellulose is one of the most abundant biopolymers in the nature and acts as a reinforcement material in plants and bacteria. Cellulose molecules have amphiphilic character and have a high density of hydroxyl groups, and consist of a chain of β-(1→4)-linked glucose residues. In recent years cellulose has been extracted from green algae, from the brown alga Laminaria and from others. This type of cellulose has unique and special properties and

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hydrophilic nature. Some bacteria belonging to the genera Gluconacetobacter, Sarcina or Agrobacterium are able to produce a particular type of cellulose, designated as bacterial cellulose.

(vi) 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.

(vii) Gellan: Gellan is secreted and extracted from the bacterium Sphingomonas elodea (previously named Pseudomonas elodea). 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.

(viii) 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 .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.

(ix) 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 .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 .

(x) Xanthan: Xanthan gum, is an polysaccharide synthesized by aerobic fermentation of the bacterium Xanthomonas campestris .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. Xanthan gum is largely the most important commercial microbial hydrocolloid used in the food industry as a thickening agent and stabilizer.

2. Proteins

(i) 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.

(ii) Gelatin: Gelatin is a protein obtained by hydrolyzing the collagen contained in bones and skin. Gelatin obtained from mammalian sources (porcine and bovine), is the most important and most used. This structure is determined by the properties of collagen from which gelatin is obtained .In the last years, in the food industry, the number of new applications for gelatin 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

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are given by the growing demand to replace synthetic agents with natural and biodegradable ones.

(iii) 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 effect. 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. Soy protein can be used in the manufacture of adhesives, plastics, and packaging materials and can be a good alternative to the petroleum polymer.

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

(v) Zein: Zein is the major storage protein of corn 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. 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.

3. Aliphatic Polyesters

(i) Polylactic acid (PLA): Poly (lactic acid) PLA, biodegradable polymers (aliphatic polyester) is obtained from agricultural products such as corn, sugarcane, and others sources. In the process of the fermentation of sugars various monomers are produced, that are converted to polymers. 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.

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 its degree of crystallinity. 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 there are microorganisms in marine environments can degrade it. PLA polymers are materials that are creating a lot of interest in the packaging industry for its properties and earth-friendly biodegradability. These properties include resistance to oil-based products, seal ability at lower temperatures, and can act as flavor or odor barriers for foodstuffs.

(ii) Polyhidroxybutyrate (PHB): Poly(3-hydroxybutyrate) (PHB) is one of the biodegradable PHA (polyhydroxyalkaoates) and is a naturally occurring β–hydroxyacid (a linear polyester).The general structure of the repeating units of these polyesters is different depending on the type of bacteria and the feed, it is typically - (CH2)n-CH3 for most naturally occurring PHAs.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. Other microorganisms that accumulate PHB are Haloferax mediterranei, Halomonas boliviensis and Bacillus megaterium.

PHB is a linear, isotactic, semicrystalline biopolymer based on (R)-3-hydroxybutyric acid.With the purpose to improve flexibility, PHB is synthesized with various co-polymers

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such as poly-(3-hydroxyvalerate) (HV) inorder to decrease of the glass transitions and melting temperature. Current applications of PHB-based polymers or composites include the packaging industry, medicine, pharmacy, agriculture, food industry.

The food industry has seen great advances in the packaging sector since its inception in the 18th century with most active and intelligent innovations occurring during the past century. These advances have led to improved food quality and safety. While some innovations have stemmed from unexpected sources, most have been driven by changing consumer preferences. The new advances have mostly focused on delaying oxidation and controlling moisture migration, microbial growth, respiration rates, and volatile flavors and aromas. This focus parallels that of food packaging distribution, which has driven change in the key areas of sustainable packaging, use of the packaging value chain relationships for competitive advantage, and the evolving role of food service packaging. Biopolymers have highly influenced the packaging sector greatly. Environmental responsibility is constantly increasing in importance to both consumers and industry.

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