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Biopolymer From Natural Rubber and Starch: A Review

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ABSTRACT

The purpose of this study is to identify the potential of starch as bio-based thermoplastic elastomers (TPEs). Starch based polymers have been recognized to have highly potential to replace existing source of conventional elastomeric polymers. The modification process of blending starch with natural rubber, plasticizers, additives, and filler contribute to the enhancement and improvement for the properties of starch in order to produce biopolymers by approaching the properties of TPEs. This research was based on the starch which is an abundant and naturally occurring polysaccharide. It used to prepare and evaluate edible biodegradable films of different starch sources namely potato starch, corn starch and oxidized corn starch. Biopolymers have been considered as the most promising materials for this purpose. Polymers that have recently attracted interest due to their highly modifiable material properties. Natural rubber obtained almost exclusively from the Para tree (*Heveabrasilliensis*) is a unique polymer in many significant applications. The use of plasticizers to process starch as thermoplastic polymer and the formulation of starch with other polymers are highlighted. Here we discuss the main results and developments innatural plasticizer/synthetic and biopolymer-based films.

Keywords: Starch; Natural Rubber; Biopolymer

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INTRODUCTION

Biopolymers based on the starch, lignin and hemi celluloses are products obtained by the degradation of starch, and other polysaccharides and sugars ¹. Starch is a natural glucose –based polymer that is generally considered as a potential candidate for future biodegradable polymer products ². To obtain useful materials from starch, the native properties must be enhanced because of starch high water sensitivity and poor mechanical properties compared to those of synthetic polymers ³. Starch and biopolymer have been chemically modified in synthetic polymers ⁴.

A large number of microorganisms produce exo polysaccharides. The structures of many polymers have now been accurately determined and some chemical structures have also correlated with the physical functions of thermoplastic starch (Tps)⁵. The biopolymers are concerned with environmental protection. Biodegradable polymers and bio composites have attracted considerable attention as green materials and biocompatible materials that will replace some or all of the synthetic plastics in many applications. The most cases, commercially available biopolymers contain a significant amount of unwanted materials that remain after the extraction process ⁶. Composite materials fabricated from agricultural products such as starch and protein powders are more biodegradable compared with those fabricated from non-agricultural products. ⁷.The use of polymers from renewable resource is environmentally advantageous alternative to synthetic polymers in application ⁸. Polymer materials are solid, non-metallic compounds with high molecular weight ⁹. They are comprised of repeating macromolecules, and have varying characteristics depending upon their composition.

Each macromolecule that comprises a polymeric material is known as a mer unit. A single mer is called a monomer, while repeating mer units are known as polymers. A variety of materials (both renewable and non-renewable) are employed as feedstock sources for modern plastic materials.¹⁰. Starch is a natural glucose based polymer that generally is considered as a potential candidate for future biodegradable polymer products ¹¹.

However most important sources for the starches are corn and cassava ¹². Chemical and physical properties of starch mainly consist of two different polysaccharides amylose and amylopectin but the ratio of these strongly varies depending on the starch source. Small amounts of lipids and proteins are also present in the starch granules ¹³. The use of natural-based biopolymer films depends on several features including cost, availability, and functional attributes, mechanical properties (strength and flexibility) ^{14, 15}.

Polymers

The preparation of biopolymers in most organic solvents has limited the applications of biopolymer based materials and composites¹⁶. Biopolymers such as cellulose, chitin, chitosin, silk and DNA can be fabricated from membranes, spheres and molded shapes. Heparin biopolymer composites are especially of interest in preparing materials with enhanced blood compatibility¹⁷. Other biopolymers studied include cellulose such as cellulose acetate, carboxyl methyl cellulose and hydroxyl propyl methyl cellulose¹⁸.

Cellulose is a linear polysaccharide of the D – glucose residues linked by β glycosides bonds, which is the most abundant renewable biopolymer on earth. It has excellent thermal and mechanical properties. Cellulose has also been applied as a membrane to protect immobilized glucose. The glucose oxidizes in biosensors are used to assay glucose in blood. Cellulose composite has been hampered by the difficulty of dissolving cellulose¹⁹.

Chitin, a co polymer unit, has been successfully used for biomedical application due to its biodegradability and monomer macro molecules²⁰. The co-polymer and N-glucosamine unit is one of the most abundant polysaccharides with an annual production just behind cellulose. Chitin forms strong intermolecular and intra molecular hydrogen bonds²¹.

Heparin a mixture of linear anionic polysaccharides having 2-O-sulfo- α -L-iduronic acid and glucose as its major repeating disaccharide and minor amounts of β -D glucuronic acid and 2 acetoamido-2-deoxy-d-glucose. Heparin is widely used as an able injects anticoagulant for acute coronary syndromes²².

Pectin is a structural hetero polysaccharide found in the primary cell wall of terrestrial plant such as sugar beet. Starch and starch derivative films have been widely studied due to the film forming properties,²³ high oxygen barrier and good mechanical strength²⁴ but have a low solubility²⁵ and the resulting film is brittle²⁶. Modified starch was used to improve the properties of film, for example, a blend of gelatin/hydroxypropyl, starch/plasticizer²⁷ and acetylated cassava starch²⁸.

Types of Polymers

Popular usage of polymer was plastic that actually refers to a large class of natural and synthetic materials with a variety of properties. The word “polymer” was derived from the Greek *poly* and *meros*, meaning many and parts, respectively. Some scientists prefer to use the word “macromolecule” or large molecule, instead of polymer³⁰. Others maintain that naturally occurring polymers, or biopolymers, and synthetic polymers should be studied in different courses. Others name these large molecules simply “giant molecules”. However, the same principles apply to all polymers.

Synthetic Polymers

Another common name for many synthetic polymers is plastic which comes from the Greek word "plastikos", suitable for molding or shaping. The synthetic polymers include synthetic rubber, Bakelite, neoprene, nylon, PVC, polystyrene, polyethylene, polypropylene, PVB, silicone, and many more³¹. Plastics have become one of the most widely used materials all over the world. Many materials in our daily use from packing, wrapping, and building materials include half of all polymers synthesized. Other uses include automotive, sport equipments, textiles, and infrastructure are made from polymers

Natural Polymers

Natural polymer was a polymer resulting from raw materials found in nature such as shellac, and natural rubber. A variety of other natural polymers exist, such as cellulose, which is the main constituent of wood and paper. Other Natural polymer was rubber (hydrocarbon base) and silicones (alternating silicon and oxygen)³².

Biodegradable polymers

Biodegradable polymers can be classified in to four categories depending on the synthesis and sources³³. Conventional plastics are resistant to biodegradation, as the surfaces in contact with the soil in which they are disposed are characteristically smooth polymers from biomass such as the agro-polymers from the resource (1) polysaccharides, e.g., starches (Wheat, potatoes, maize)³⁴. Ligno-cellulosic products (wood, straws)³⁵ and others (pectin, chitosan /chitin, gums)³⁶. Protein and lipids, produced from animals (casein, whey, collagen/gelatin)³⁷ and plants sources zein, soya and gluten³⁸.

The second class of polymer materials under consideration is partially degradable material³⁹. They are designed with the goal of more rapid degradation on conventional synthetic plastics⁴⁰. Production of this class of materials typically includes surrounding naturally produced fibers with a conventional (petroleum based) matrix⁴¹.

The final class of polymer materials is currently attracting a great deal of attention from researchers and industry⁴². These plastics are designed to be completely biodegradable. Polymers chemically synthesized using monomers obtained from agro resource⁴³. Only the last category is obtained from non-renewable resources recent innovation in edible and biodegradable polymer films are widely discussed in the literature presenting improvements in the food packaging, surgery, pharmaceutical uses⁴⁴.

All the biopolymers are synthesized by enzymatic processes in the cytoplasm, in the various compartments or organelles of cells, at the cytoplasmic membrane or at cell wall components, at

the surface of cells or even extracellular, synthesis of a biopolymer may be initiated in one part of a cell and may be continued in another part as it occurs⁴⁵.

Production of biopolymers

There are different ways to produce biopolymers in order to make them available for different applications. Many biopolymers occur in nature and are isolated from plants and algae. Then grow in a natural environment. Many biopolymers occur abundantly in nature and are isolated from plants and algae, which grow in natural environments. Agar and alginates are isolated from red algae belonging to the genus *Gelidium* or from various brown algae also referred to as seaweeds. Few biopolymers are isolated from extremely natural sources. An example of such an exception is hyaluronic acid, which is extracted from the umbilical cords of new born children. In vitro synthesis of biopolymers with isolated enzymes in cell-free systems offers another possibility to produce biopolymers⁴⁶. One example is the application of the heat stable DNA polymerases in the polymerase chain reaction (PCR) to produce monodisperse defined DNA molecules. Another example is dextran, which can be produced on a technical scale with isolated dextran sucrose⁴⁷. Production of raw material is carried out through fermentation. In their final stage of preparation, they can be processed by standard extrusion and molding techniques.

Use of Natural Extracts in biodegradable Polymers

Different natural compounds have been proposed for incorporation polymer metrics. It is used to improve the packaging functionalities as well as the food quality and safety⁴⁸. The demand for the use of natural additives in formulations of polymer has produced in recent years a clear increase in the number of studies based on natural extracts which come from plants essential oils or agricultural waste products. A large number of studies have described the broad antimicrobial spectrum against different pathogenic and spoilage microorganisms including gram negative and gram positive bacteria and molds. Different types of biopolymers can be used in the development of antimicrobial active films to develop antimicrobial activity⁴⁹.

Natural Rubber

Natural rubber is the most important material and most widely used in expansive applications⁵⁰. Natural rubber has high strength as a vulcanizer (cured, low hardness rubber, containing no filler, but it is soft and low dimension stability⁵¹. Natural rubber (NR) is widely used in industry and is freely and naturally available at low expense⁵². The natural rubber has been used widely in segments as transportation and health. It is currently used in different products such as: adhesives, wires, surgical gloves, health equipment and accessories, condoms, coatings, and floor covering.

Natural rubber is an important material because it cannot be replaced by synthetic rubbers in some applications, due to its outstanding⁵³.

The natural rubber latex is extracted from the rubber tree (*Heveabrasiliensis*) a plant originated in the Amazon rainforests. The latex is a colloidal dispersion of rubber particles, sizing from 500-3000 nm in aqueous serum. For logistic reasons, the latex is usually dried to rubber or stabilized (with ammonia and other substances) and concentrated by centrifugation to a solid content of 70%⁵⁴.

Natural rubber it is estimated that there are more than 2000 species of trees, shrubs, or vines from mostly tropical and also temperate climate regions that produces milky fluid that congeals when exposed to air or known as latex from which natural rubber or a closely related material can be obtained. Only important commercial source of natural rubber many plant species produce rubber. Natural rubber is obtained from the *HeveaBrasiliensis* tree by cutting a thin slice of the tree bark with a trapping knife. This process is called tree trapping⁵⁵. About two to three hours after tree trapping, the latex collected from the trees are then added with ammonia to prevent coagulation, and brought to a factory or centre. The tapped latex consists, rubber, proteins, amino acids, starch, sterols, esters and salts⁵⁶.

To prevent degradation, antioxidants have to be added as soon as the rubber is exposed to oxygen. Due to the large uncertainties in the processing it is not possible to calculate the economic and environmental impact of the processing steps. Production of one ton of natural rubber from *Hevea* requires mainly for transport of the material⁵⁷.

Starch

Starch is the principle carbohydrate storage product of higher plants. The term starch actually refers to a class of materials with a wide range of structures and properties⁵⁸. Starch polymers can be extracted from corn, potatoes, rice, barley, sorghum and wheat. The principle source of the starch for industrial and food purpose is corn⁵⁹. Starches are mixtures of two glucan polymers, amylose and amylopectin. These polymers are accumulated in plant as insoluble energy storage granules, with each granule containing a mixture two polymers. This is important because amylose and amylopectin have different properties and applications⁶⁰. Starch is a natural glucose based polymer that generally is considered as a potential candidate for future biodegradable polymer products. Starch is extracted from various plant tissues⁶¹.

Starch films can be produced by extrusion or casting⁶². The thermal processing of starch based polymers involves multiple chemical and physical reactions like water diffusion, granule expansion melting and crystallization. The starch decomposition temperature is higher than its pre

gelatinization melting temperature. Starch has a high glass transition temperature. The properties of plasticized starch depend very much on moisture content. Reductive humidity changes the material properties through a and sorption desorption mechanism ⁶³.

Thermoplastic starch Research and development on biodegradable plastics is stimulated due to rising oil prices and further augmented by environmental concerns. Pure starch is highly brittle, and has poor mechanical properties and stability is offered by reinforced fibers or blended with synthetic polymers ⁶⁴. Blends of starch with thermoplastic polymers have been prepared in the past ⁶⁵.

Starch and starch derivatives

Green plants such as potato, rice, maize (corn), and cassava are raw materials for production of biopolymers. The main component of these plants is starch. Starch is considered a potential polymer to be used in biodegradable materials because of its low cost, availability, and because it is produced from renewable resources ⁶⁶. Starch is mixture of two D-glucan homo polymers, composed of a-D-glucopyransosyl units (AGU), namely, amylose and amylopectin. Molecular weight of amylose depends on the starch origin ⁶⁷. Generally, amylose extracted from cereals has lower molecular weight. Starch which is an abundant and naturally occurring polysaccharide was used to prepare and evaluate edible biodegradable films ⁶⁸.

Starch – based plastics

The use of starch in the manufacturing of a bio plastics began in the ⁷⁰ s due to its advantages, such as the starch is cheap, abundant and renewable. Besides, it is found in their several forms due to the origin of its raw material. In the granular state, it has been used as filling agent for polyolefin and as a component in synthetic polymers blends. Starches have also been modified by means of “grafting” with vinyl monomer. It is possible to produce starch films through the grafting of polymers, such as polyethylene (PE). Starch is biodegradable and these films are practically no longer used. Silane with a general formula of $\text{CH}_3\text{-Si-O-(R1, R2, R3)}$ can be added to a blend of PE to improve the compatibility of these two materials.

Thermoplastic starch (TPS)

The TPS is a relatively new concept and it is one of the main research hints for the manufacturing of biodegradable materials ⁶⁹. The starch is not a real thermoplastic, but, in the presence of a plasticizer (water, glycerin, sorbitol, etc.), high temperatures (90-180°C) and shearing it melts and fluidizes, enabling its use in injection, extrusion and blowing equipment such as those for synthetic plastics ⁷⁰. The water added to the formula plays two roles: it is an agent that breaks the structure of the native granule, breaking the bonds of hydrogen chains, and it is a plasticizer ⁷¹. This material

can be processed in the same way as synthetic materials: extrusion, injection, etc.⁷². Plasticizer such as glycerol, sorbitol etc. is added in a ratio ranging from 20% to 40% to the starch weight 30 g⁷³. The plasticizer content is directly related to the mechanical properties and glassy transition of the material⁷⁴. Polymers can be blended with the starch or applied to multilayered films, with an internal layer of starch and two external layers of impermeable polymer⁷⁵.

CONCLUSION

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. Biopolymers can be used for the preparation of edible films which is inexpensive if prepared from natural raw materials. Biopolymers has a wide range of applications. There are many difficulties in the processing of bio based polymers which can be overcome only by extensive research.

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