

Application of Polysaccharides in Biodegradable Films

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Biodegradable films emerge as alternative biomaterials to conventional packaging from fossil sources, which, in addition to offering protection and increasing the shelf life of food products, are ecologically sustainable. The materials mostly used in their formulation are based on natural polysaccharides, plasticizing agents, and bioactive components (e.g., antimicrobial agents or antioxidants). The formulation of biodegradable films from polysaccharides and various plasticizers represents an alternative for primary packaging that can be assigned to specific food products, which opens the possibility of having multiple options of biodegradable films for the same product.

polysaccharides

natural polymers

biodegradable films

1. Introduction

Polysaccharides are the most abundant natural polymer on Earth, which are composed of 10 or more repeating units of monomeric sugars that are linked by glycosidic bonds ^[1]. These biological macromolecules have vital functions (e.g., structure and energy production) in the organisms that possess them; however, their importance for human beings is due to their functional properties demonstrated, e.g., as antitumor and antioxidant agents, as well as regulators of intestinal flora ^[2].

In the industry, polysaccharides are valuable because they are a potential replacement for petroleum-based polymers; however, it is known that their application has not been fully exploited, despite their versatility ^[3]. The study by Souza et al. ^[4] revealed that the use and application of these natural materials has grown by 17% in recent years (2017–2021), which is equivalent to a world market of up to 10 billion USD; in addition, it is expected that, at the end of this decade (2030), this market will be more than 22 billion USD. In this sense, there is interest in testing alternative polysaccharide extraction processes that improve yields or provide purer extractions, as well as alternative sources (e.g., residues) to extract new polysaccharides ^[4].

A biodegradable film is considered a primary packaging made of biodegradable polymers, particularly polysaccharides, which has advantages over synthetic packaging ^[5]; specifically, it can preserve of quality and extend the shelf life of the minimally processed products ^{[6][7]} without damaging or altering the environment ^[8].

2. Sources and Characteristics of Polysaccharides

2.1. Plant Polysaccharides

Plant polysaccharides are macromolecules composed of identical or different monosaccharides linked by α or β glycosidic bonds [9]. This class of polysaccharides is divided into two categories according to their functionality, storage, and structure; the first category encompasses polymers that are part of the energy reserves of plants, while the second category encompasses those that are part of the cell walls in such a way that they confer rigidity and flexibility to the plant [10].

2.2. Algal Polysaccharides

Polysaccharides are the most abundant macromolecules in the structure of algae, since they are found as mucopolysaccharides, i.e., structural and energy storage molecules [11]. Although between 4% and 76% of the dry weight of algae corresponds to polysaccharides, the content varies depending on the species of algae; for example, green algae have lignin, cellulose, and hemicellulose, brown algae have only cellulose, and red algae are made of dietary fiber [12].

2.3. Animal Polysaccharides

Animal polysaccharides are considered natural biopolymers due to their biodegradability, biocompatibility, nontoxicity, and non-antigenicity. Furthermore, these biological macromolecules play a structural and storage role in animals, since they are part of the tissues and cell matrix, and they are a source of energy. These polysaccharides can be divided into chitins and glycosaminoglycans [13][14].

2.4. Bacterial Polysaccharides

Bacterial polysaccharides are natural biopolymers made up of monosaccharide chains, which, depending on the type of chain, have rheological, biological, and physicochemical properties. These molecules are valued for their viscous, thickening, stabilizing, and gelling properties, in addition to their antitumor, anti-inflammatory, and antimicrobial activities [15]. The production of bacterial polysaccharides can be carried out in two ways, extracellularly and intracellularly, depending on the substrates and requirements of the bacteria [16].

2.5. Fungal Polysaccharides

Fungal polysaccharides are found in the cell wall or are formed from energetic processes in edible fungi and yeasts [17]. They are polymeric molecules with linear and branched structures that are composed of homo- and heteropolysaccharides that can be joined by β -(1–3), β -(1–6), or α -(1–3) bonds, resulting in complex structures with different characteristics. For example, the antitumor activity of these polysaccharides is known to be influenced by the spatial conformation of the molecule, the degree of branching, and the molecular mass [18].

3. Biodegradable Films

Biodegradable films and coatings are solid matrices formed by crosslinking between polymers and additives (e.g., plasticizers and crosslinking agents) [19][20]; however, it is important to identify the difference between both. Coatings are generated directly on the product by spraying or immersion techniques, while films are pre-generated before covering the product [21] by casting, extrusion, or electrospinning techniques [22]. The main method for the generation of biodegradable films is the casting technique [23], in which a dispersion between compounds (i.e., polymers and additives) is generated with a volatile solvent, which is poured into a smooth mold and left to stand until the solvent evaporates [24].

3.1. Characteristics and Properties of Biodegradable Films

Biodegradable films are an alternative that the packaging industry has targeted, particularly for food packaging. Therefore, the function of biodegradable films is not to completely replace synthetic packaging, but to mitigate the environmental impact generated by solid waste [25] and provide a benefit to food by intervening in its useful life [5][26]. Therefore, biodegradable films must meet the following requirements and characteristics so that they can be functional [23][27]:

- (1) prevent or mitigate mechanical damage,
- (2) prevent or reduce lipid oxidation,
- (3) prevent or reduce microbial spoilage,
- (4) control oxygen absorption,
- (5) generate a selective barrier to carbon dioxide and water vapor,
- (6) regulate the generation of ethylene to delay senescence,
- (7) regulate the release of food additives (e.g., antioxidants, dyes, and flavors).

Biodegradable films require at least one polymeric component, based on lipids (e.g., waxes, fatty acids, and acylglycerol), proteins (e.g., caseins, whey protein, and zeins), polysaccharides (e.g., cellulose, starch, and gums), or their mixtures [8]. In addition, additives (such as plasticizers and surfactants) to modify the intermolecular bonds between polymers can be incorporated, or even bioactive compounds with fungicide, herbicide, and antioxidant capacity (e.g., natural extracts) to inhibit the development and spread of pathogenic microorganisms [28][29][30][31]. Accordingly, the thickening, gelling, and emulsifying properties of the dispersion, the texture of the matrix during polymerization, the cohesion and assembly when dehydrated, and the organoleptic and mechanical characteristics in the final film are improved [20][32][33][34][35][36]. However, not all polymers have the intrinsic properties suitable for use in the production of biodegradable films [37].

Polysaccharides are the most used polymers in the formulation of packaging materials for food preservation, due to their low cost and accessibility; however, the choice of polysaccharides in the formulation of biodegradable films is preferred due to the easy modification of nature hydrophilic with additives, which is reflected in its mechanical and barrier properties [8].

The efficiency of barrier properties such as water vapor permeability (WVP), ethylene content, and oxygen level maintain control of the transfer of ambient moisture and volatile components (e.g., aromas and flavors) [38], which influence the food preservation [39], dehydration of fresh products, hydration of dry products, or oxidation of polyunsaturated fats in food [8]. On the other hand, mechanical properties such as tensile strength (TS), elongation at break (EB), and young modulus (E) are related to the integrity and brittleness of films during handling and storage [40]. Some investigations reported that mechanical properties improved with the incorporation of hydrophobic additives (e.g., glycerol or sorbitol) [41]. Physicochemical characteristics such as color, opacity, luminosity, morphology, and roughness are directly related to the type and concentration of polysaccharides, as well as the film-making method [42][43].

4. Biodegradable Films Based on Polysaccharides

4.1. Biodegradable Films Based on Starches

Starch-based biodegradable films are the most studied because they are considered isotropic, colorless, tasteless, odorless, nontoxic, and biologically degradable [44]; however, the hydrophilic nature of starch requires proper formulation to generate functional films (i.e., mechanical strength) with control over water content and WVP [45]. However, the source of production has an influence on the mechanical and barrier properties, due to the fact that, by their nature, starch films have good WVP, but mechanical properties depend on the crystallinity of the starch used [8].

4.2. Biodegradable Films Based on Celluloses and Derivates

Celluloses are used in various food packaging materials because they are versatile, low-cost, and nontoxic, and they have excellent mechanical properties. For example, cellophane is the most widely used cellulose derivative in packaging; however, its formulation with synthetic materials classifies it as a highly polluting material [46]. There are other natural derivatives of cellulose that are used in the formulation of biodegradable films, such as carboxymethyl cellulose, cellulose regenerate, and some cellulose esters (e.g., cellulose acetate, palmitate, and octanoate). Films generated with cellulose or their derivatives are flexible and moderately resistant, with efficient WVP; however, these properties vary depending on the hydrophobicity and crystallinity modification caused by the incorporated additives [8].

4.3. Biodegradable Films Based on Pectins

Pectin-based biodegradable films are the natural material proposals that have presented the most disadvantages, due to their fragile nature and poor WVP and mechanical properties; however, these films have a positive influence with the addition of plasticizing agents [47]. For example, Shafie et al. [48] and Gouveia et al. [47] generated biodegradable pectin films; in the first study, no plasticizer was used, while, in the second study, glycerol was evaluated. The films with glycerol showed an evident increase in ST, but a decrease in EB. Such an effect is contrary to what happens to cellulose films with the addition of glycerol; however, it is not a recurrent result in pectin films. In previous studies [49], the effect of increasing glycerol concentration in pectin films was evaluated, and the results were consistent with a decrease in TS and an increase in EB (as in cellulose-based biodegradable films).

4.4. Biodegradable Films Based on Gums

Gums are defined as hydrocolloids due to their properties as emulsifiers, stabilizers, texturizers, thickeners, coating agents, and film generators; however, their potential application depends on the type of gum and its source [50]. The gums most used as film-forming agents are guar, gellan, xanthan, Persian, konjac glucomannan, and Arabic gums; however, the study carried out by Pedreiro et al. [51] established that their main application is as a coating applied directly (by immersion or dipping) on the surface of foods (e.g., tomatoes, guavas, mangoes, and mushrooms) because they are GRAS, they can perfectly incorporate bioactive compounds (e.g., extracts or antimicrobial agents) and extend the shelf life of products [51].

4.5. Biodegradable Films Based on Agars

Agar is easy to extract, safe, and cheap, making it a profitable polysaccharide for biodegradable film formation [52]. The formation of the agar matrix results from the intermolecular interaction of hydrogens of agarose with water molecules; in addition, its properties allow it to interact with bioactive substances such as antimicrobials [53]. According to Mostafavi and Zaeim [54], the greatest limitations of biodegradable agar films are their fragility, low elasticity, high solubility, low thermal stability, and high permeability; therefore, one solution is to incorporate other polysaccharides and plasticizing agents. However, in general, the mechanical (i.e., TS and EB) and barrier properties are relatively low (compared to starch films). Furthermore, the incorporation of plasticizers does not significantly increase the values.

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