Chapter

Biodegradable Polymers: Opportunities and Challenges

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Abstract

The overuse of polymer materials from fossil sources has generated a large volume of waste that causes environmental impacts due to the degradation time. The technological advance has stimulated the search for alternatives that can contribute to sustainability. In this context, the use of biodegradable polymers, that use raw materials from renewable sources stand out because they have that ability to form films and come from abundant sources. Also, in the expectation of optimizing the environmental benefits in this process, it is possible to value the agroindustrial residues, using them as raw material in the synthesis of the polymer, the physical, chemical and mechanical properties of these polymers are important to evaluate the possible applications. The proposal of this chapter is to present current research on renewable sources, including agricultural and industrial residues, to obtain biodegradable polymers, highlighting their properties and possibilities of application.

Keywords: sustainability, waste, biodegradable, renewable, agroindustrial

1. Introduction

The increasing environmental impacts of pollution derived from fossil polymers are drawing attention to the need to produce sustainable materials. And the biodegradable polymers generated from renewable sources are an alternative to this problem [1]. They are made from renewable or synthetic sources that have the capacity to degrade by the action of microorganisms [2, 3].

In the search for biodegradable and renewable materials, the biopolymers that are gaining prominence are those that have greater availability: cellulose, chitosan, starch and proteins (collagen, soy, casein). As these sources are widely used in the food, pharmaceutical, agricultural, and other industries, material research has been developing in the quest to recover them from agroindustrial waste. These could be reinserted into the process as a source for synthesizing biodegradable polymers, as both industries and agriculture generate waste that is sometimes incorrectly disposed of in the environment.

Residues and by-products generated in larger quantities include fruit and vegetable residues (husks, seeds and stems), grain residues (rice, wheat, soy) and protein products (chitosan, gelatin, whey protein) [4]. Approximately 26% of food waste is generated from the beverage industry, followed by the dairy industry (21%), fruit and vegetables (14.8%), cereals processing (12.9%), preservation of meat products (8%), processing of oils of vegetable and animal origin (3.9%), among others (12.7%) [5].

The use of residues is seen as an opportunity for sustainability due to its ease of production and low cost, non-toxicity, biocompatibility, biodegradability, chemical and thermal stabilities [6]. Associated with the concern to replace materials of fossil origin, attention to the reuse of wastes/by-products of agricultural or agroindustrial origin is of extreme importance. In this way, in addition to contributing to the reduction of disposal of waste in landfills or the burning of landfills, the principle of reuse affects the economy in a positive way.

Despite these advantages, the water absorption is very high, due to the number of hydrophilic groups contained in the structure of the materials of renewable origin. To overcome this factor, techniques have been applied to improve the physical and mechanical properties of these materials, ensuring a better application performance. In addition, there is still a large gap between policy and implementation of these new technologies [7].

The following sections discuss the main sources of biodegradable polymers, aiming to know their specificities, so that to facilitate the link between possible sources to obtain them from agricultural or industrial waste, as well as the applicability of the material.

2. Sources for obtaining biodegradable polymers: opportunities

In the search for biodegradable and renewable materials, the biopolymers that are gaining prominence are those that present greater availability: cellulose, chitosan, starch and proteins.

These sources are widely used in the food, pharmaceutical and agricultural industries, causing the generation of large amounts of waste. This problem has aroused interest in research aimed at obtaining biopolymers from the recovery of the same, relating low cost, availability and sustainability.

2.1 Cellulose

Cellulose is the agroindustrial waste most reuse. Its main sources of production are mainly of vegetal origin (wood and cotton), however, it is also synthesized by algae, tunicates and some bacteria [8–10].

The cellulose molecule ($(C_6H_{10}O_5)_n$) has a linear ribbon-like conformation, and its compounds bound together by the so-called $\beta_{1\text{-}4}$, glycosidic bonds. The number of chain repeats n varying according to the source of the obtainment, wherein in wood, for example, is about 10,000 and 15,000 in cotton. These chains impart rigidity to the cellulose, providing good mechanical properties and thermal stability. However, cellulose dissolution is a difficult process and it is necessary to develop new techniques that allow the use of regenerated cellulose as a component of polymeric materials [11, 12].

The materials produced from regenerated cellulose acquire exceptional physical and chemical characteristics, as well as clear benefits for society, especially when minimizing environmental impacts. During the regeneration of the cellulose solution, physical and chemical treatments can be applied generating functional and biocompatible materials, organic hybrids or porous membranes, making the use of cellulose comprehensive [12].

In this sense, the cellulose modification has been the focus of several studies, aiming to evaluate it as a substitute raw material to obtain synthetic polymers, fibers, films and membranes, hydrogels and aerogels, bioplastics, beads and microspheres as shown in (**Table 1**).

Author	Objective of study
Fibers	
[13]	Obtaining of magnetically activated cellulose fibers by moist spinning cellulose/ Fe_3O_4 solution in 1-ethyl-3-methylimidazolium chloride.
[14]	Manufacture of regenerated cellulose multifilaments by means of pilot scale spinning equipment from the cellulose solution in NaOH/Urea.
Films and membranes	
[15]	Development of new cellulose films via low temperature solvents.
[16]	Manufacture of flexible, transparent and fortified regenerated films by crosslinking the cellulose with epichlorohydrin (ECH) in NaOH/Urea.
[17]	New method of preparation of hydrated membranes of cellulose in NaOH/Urea, employing a process of pregelatinization.
[18]	Direct production of films with cellulose nanocomposites from cellulose microfibers using nano-soldering based on ionic liquid.
[10]	Manufacture of optically clear paper from densely packed cellulose nanofibers.
Hydrogels and aerogels	
[19]	Manufacture of a series of cellulose hydrogels directly from the cellulose solution followed by crosslinking with epichlorohydrin (ECH) via heating and freezing.
[20]	Production of regenerated cellulose hydrogels made from lithium chloride/ dimethylacetamide by slow coagulation with water.
[21]	Preparation of hydrogel from a cellulose solution in an ionic liquid of 1-butyl-3-methylimidazolium chloride and water at room temperature.
[22]	Carbonized aerogels after pyrolysis under nitrogen flow and doping with platinum nanoparticles.
Beads and microspheres	
[23]	Manufacture of cellulose beads from thin plates of Cellulose/NaOH solution in a water bath.
[24]	Preparation of macroporous spheres with viscose cellulose xanthogenate densified with high density tungsten carbide via thermal regeneration in water-in-oil suspension with starch as a porogenic.
Bioplastics	
[25]	Construction of new cellulose bioplastics (CBP) from cellulose hydrogels prepared by cellulose solution in NaOH/Urea via simple hot pressing.

Table 1.
Studies to obtain materials with cellulose in its composition.

Recent studies have turned their efforts to provide reuse and value adding to industrial waste. In order to convert lignocellulosic materials into nanocellulose, [26] used the residues of tobacco stalks after steam blasting followed by bleaching and refining to produce nanofibrillated cellulose (NFC), successfully reaching the objective of the study, and generating a promising alternative for the reuse of this residue organic.

Reference [27] extracted microcrystalline cellulose (MCC) and spherical nanocrystalline cellulose (SNCC) by acid hydrolysis from cotton fabric waste, concluding that the developed process is suitable for industrial scale application, since the generation of cotton waste is high, as well as the cellulose content contained in them (about 94%).

Reference [28] isolated microcrystalline cellulose powder (MCC) from waste paper from three sources (books, newspapers and cardboard), evaluating the effect of the treatment using various concentrations of sodium hydroxide (NaOH) on the properties of the powders obtained, concluding that the lowest concentration, which was 5% (m/v) NaOH in the medium, was ideal for MCC isolation in these paper wastes.

Aiming to reduce the environmental impacts caused in aquatic life due to the contamination of water by complex substances such as petroleum and vegetable oils, [29] developed a hydrophobic aerogel with high sorption capacity, from cellulose nanofibres obtained from waste from the furniture industry, processed via acidic hydrolysis by steam explosion for oil sorption. The authors tested the sorption capacity of the aerogel produced in homogeneous media (pure oil and vegetable oil) and heterogeneous medium (oil in water), where it had high sorption capacity in both media, 19.55 and 19.21 $g_{oil}\ g_{aerogel}^{-1}$, for petroleum and oil respectively.

2.2 Chitosan

The chitosan is a molecule with a carbohydrate structure like cellulose, consisting of two types of repeating units, N-acetyl-D-glucosamine and D-glucosamine, linked by $\beta_{1\text{-}4}$ glycosidic bonds [30]. They are the most abundant organic compounds after cellulose [31].

It is widely distributed in the animal kingdom (shells of crustaceans and mollusks, the backbone of squid and the cuticle of insects) and vegetable (algae, protozoa and the cell wall of several fungal species) [32].

The degree of acetylation differentiates chitin from chitosan, when the polymer has a degree of acetylation greater than 50%, is called chitin, and when the degree of acetylation is less than 50%, it is called chitosan [33].

Reference [34] discuss the main methods of chitosan extraction, measure alkaline treatment, which is most commonly used at the industrial level, and sodium hydroxide (NaOH), which is commonly used for the deacetylation process. The enzymatic deacetylation that uses chitin deacetylases obtained from different biological sources, such as fungi and insects to effect treatment. And steam explosion, which performs a hydrothermal treatment where the chitin is treated with a blow gun, with saturation vapor at increased pressure and temperature for several minutes, followed by explosive decomposition.

There are several studies that provide application opportunities for a chitosan. For the food area: active films, antioxidants, antimicrobials, chitosan compounds, edible coatings, application in fruits and vegetables and application in seafood products [35]. [36] made a comparison between nano-composite films based on gelatin and starch modified by nanocellulose and chitosan for packaging applications. And [37] developed and evaluated an antioxidant film and pH indicator based on sources of chitosan and food waste. [38] incorporated the extract of mango leaves to the antioxidant film of chitosan for active food packaging.

In addition, it can be used in a number of areas, such as biomedicine, pharmaceuticals, food, agriculture, personal care products and the environmental sector [39]. [40] developed nanoparticles of chitosan coating for the treatment of brain diseases. [41] studied nanogels of chitosan as nanocarriers of polyoxometalates for breast cancer therapies. In the environmental area [41] have developed a lysozyme-chitosan biocomposite for the effective removal of dyes and heavy metals from aqueous solutions. [42] have made antibacterial and ecologically correct membranes of chitosan and polyvinyl alcohol for air filtration. In the area of agriculture [43] chitosan nanoparticle delivery systems for sustainable agriculture and [44] biocompatible chitosan nanoparticles loaded with agrochemicals for pest management.

However, there is a great waste of chitosan in marine waste from processing industries, there has been a significant increase in recent years, due to modern seafood processing practices that result in the accumulation of a large volume of waste (skin, head, tails, shells, scales, spine). As the rate of biodegradation of this material is low because chitin is not soluble in water, this volume accumulates and consequently causing environmental impacts. [45, 46].

These marine residues are potential materials for extracting chitin and chitosan. This requires the recovery of chitosan present in these wastes. [47] extract and characterize the fish scale chitosan (*Labeo rohita*). While [48] make the extraction from abundant shrimp residues (exoskeleton - shells). Already [49] use as extraction source the blue crab. And [50] performed alkaline hydrolysis to recover the chitin and chitosan from the squid feather and used the residual water of this process to recover the proteins and evaluate the antioxidant action.

The challenge is to obtain materials with properties equivalent to fully synthetic products [45]. Since, in the preparation of films, for example, when only chitosan is used, there are disadvantages as poor mechanical and barrier properties due to the absorption of moisture [51]. The ideal would be to use materials that add these absent characteristics.

2.3 Starch

Starch can be found in many vegetables in the granule formula and its composition is basically from two polysaccharides: amylose (linear) and amylopectin (branched) [52]. It is one among foods that have significant energy source in the human diet. In addition to the use for consumption, the starch can be used for pharmaceutical and functional purposes and is widely used for its desirable physicochemical properties such as grain swelling, viscosity, gel formation capacity and water binding affinity [53].

The modification in the structure of starches is closely linked to the process of retrogradation, which generates a reorganization of the molecules present. Research on this phenomenon generally occurs in aqueous dispersions at different concentrations. Other factors that may be associated in the modification of starch are the disorganization and rupture of the granules, which occur in the presence of high temperatures [54].

When the starch is heated at a characteristic temperature called the gelatinization temperature (60–70°C) in aqueous solution, the swelling step of the grain occurs, where the amylose is solubilized. At temperatures lower than 100°C and without mechanical shear the granules have their integral structure and are characterized as viscoelastic [52].

In order to obtain improvements in starch properties, as well as to solve some problems, starch modification has occurred, that can occur genetically, physically, chemically or even enzymatically [55].

With genetically modified starches there are opportunities for starch production with improved functionality, for example with high levels of amylose and phosphates, with amylopectin short chains without the presence of amylose, and as properties one can mention stability to freezing and thawing [55].

As an example of physical modifications, high pressure homogenization has resulted in a physically modified starch having crystallinity reduction properties in the starch grain that could produce a hydrogel with stronger gel networks [56]. Modification by treatment of humidity and heat that generates interactions and new associations between the amylose and amylopectin structures, besides the ultrasound that can also be used as a physical method for the modification of starches [57].

Among the chemical modifications it is important to mention acid hydrolysis, acetylation, esterification, double modification and oxidation. The purpose of the chemical modification is to replace a new functional group that would add desired properties to the starch [58].

The modification of starch through enzymes mainly involves the use of hydrolyzing enzymes, an important aspect is that the enzyme must be free of components that can cause damage to starch molecules [39].

The starch after conversion into thermoplastic presents itself as an alternative for the replacement of polymers of fossil origin, mainly in relation to the properties and biodegradability of the final product. Further, on starch thermoplastic studies show that the higher proportion of amylose to amylopectin provides more flexibility and makes it even more thermoplastic [59].

Since starch can come from a variety of plant sources, it is therefore comprehensive and has high availability, recent studies highlight the use of this biopolymer through alternative sources such as starch recovery or reuse of waste in various applications, such as residual starch from the milling process, or maize residues to obtain bioethanol [60, 61] and applications as biodegradable films as shown in **Table 2**.

2.4 Proteins

Proteins are polymers of natural origin, consisting of peptide bonds, the result of hydrogen bonds, ionic bonds and cross-links between amines that can originate from plant or animal material [67]. Some examples of proteins that are used as substitution of polymers of petroleum origin are: soy protein, casein, collagen and some others not so used, as wheat gluten and ovalbumin, due to the low availability of the material [68].

2.4.1 Collagen

Collagen is a natural protein present in animals and is responsible for ensuring the structure that supports the skin and organs. Beyond the skins, it can be found in bones, cartilage and some other structures. Formed by amino acids, the collagen is structured by a helix triple consisting of proline, hydroxyproline and glycine molecules [69].

Author	Objective of study
[60]	To evaluate ethanol production by *Zymomonas mobilis* ZM4 and an industrial ethanol producing strain of *Saccharomyces cerevisiae* using as substrate residual starch of wet flour milling, supplemented with crushed wheat grains, with subsequent hydrolysis.
[61]	The residue flow of potato starch produced during chip manufacturing was used as an economical source to produce biomass and bioethanol by *Saccharomyces cerevisiae.*
[62]	Production of biodegradable films based on thermoplastic corn starch and starch extraction residues from *Pachyrhizus ahipa.*
[63]	Mechanical and chemical treatment of turmeric residue, aiming application in the production of films with improved properties.
[64]	Extraction and characterization of pineapple stems using common mechanical extraction with water.
[65]	The production of ethanol using as raw material an agroindustrial residue rich in complex starches, called thippi, which after combined treatment with steam and enzymatic hydrolysis, was subjected to mixed culture fermentation.
[66]	Recovery of mixed biopolymers composed of starch and curcuminoids from the extraction of supercritical fluid and pressurized liquid.

Table 2.
Studies from recovered starch.

The origin of this collagen can be derived from residues from slaughterhouses, as well as from fishing activities [70]. The volume of waste from these activities can generate high environmental impact, since there is very little reuse on them. Thus, their destination is usually for landfills, or mostly, in irregular deposits in nature, contributing to contamination of soil and water resources. The high volume and little reuse can be justified by the leftovers during the processing of the raw material and low commercial value of the by-products generated.

Collagen, in its natural form, has little application. Therefore, one chooses to extract the gelatin present in its composition for use. In order to obtain the gelatin, it is necessary for the collagen to undergo a hydrolysis process (acidic, alkaline or enzymatic), associated with high temperatures, to break the covalent bonds, releasing the gelatin molecules, through denaturation of the helix triple. After cooling the solution, the chains absorb the water, forming gelatin [69].

Gelatin is the result of water-soluble proteins, that after extraction, can be purified and concentrated, eliminating some salts or undesirable substances contained in its structure that may compromise its application. This is another factor that may imply its applicability, generating a water absorption in the material larger than the desired one. Depending on the origin of the residue, salts such as chromium and sodium can be found (residues of leather trimmings, for example). The presence of magnesium and chlorine can be observed due to alkaline or acidic hydrolysis, respectively, that was employed in the gelatin extraction process.

Collagen and gelatin are considered good materials for application in several areas, including medical, pharmaceutical and cosmetic areas [71]. For application in the health area, purification should be more complex, involving filtration steps, generally carried out by ultrafiltration membranes.

For the food area, as referred in films for food coating, gelatin extracted from fish waste (bone and cartilage) can be used without contraindications, however gelatin extracted from tanning waste leather is not allowed for use by legislation, due to chrome remnants that exist in the solution. Gelatin from leather residue can be reused to produce films for soil cover [72]. Studies on the use of this polymer for cover application have been increasing, due to the fact of the optimum biodegradability of the material.

For the leather waste there are also other alternatives, besides the use for extraction of gelatin. Many authors have studied its use as fertilizer, due to its high potential for containing nitrogen content in its composition [73]. For use as fertilizers, the residue can be treated by adding more essential mineral salts to the soil with phosphorus and potassium.

2.4.2 Soybean

Soybean is the main grain marketed in the world and is used in many processes to obtain different consumer goods. Because it is widely applied in the industry, it is also capable of generating a lot of waste. Soybean meal, considered as a by-product of the extraction of oil contained in grain for food production or biofuel, is mainly destined for animal feed [74].

Protein isolate from soybean has been the subject of many studies. Despite its high protein content, its reuse is restricted due to its high stiffness and low water resistance [75]. Materials that use soy protein have great potential for replacement of polymers of fossil origin. It can be used as an adhesive for food coatings, as packaging for use in horticulture, guaranteeing its function as both container and fertilizer [76].

When used as a base for packaging manufacture, the soy protein isolate has good advantages such as biodegradability and good gas barrier property. However, its low tensile strength makes its application difficult [77].

Techniques such as coatings and crosslinking are applied to the polymer matrix, resulting in a material with improved mechanical properties, as well as increasing the shelf life of the film.

The coating, when employed, provides low water permeability, while the crosslinking technique provides better mechanical properties when compared to the coating. In addition, it can be seen that the amount of hydrophilic groups is reduced.

Although it is shown as a more efficient technique, the crosslinking uses agents that can present certain toxicity, limiting its application in the food industry [75]. Thus, it is sought to use biological macromolecular materials, such as starch, chitosan, cellulose, for the formation of films [78].

2.4.3 Casein

Casein is the protein found in milk, of high nutritional value. It can be found in one of the residues that in recent years have generated many problems for dairy products: whey. Despite this being used in dairy production with its due treatment, was once considered as a by-product in the food industry.

Casein can be used in films for food coatings and pharmaceuticals, its main application despite the few studies on its excellent characteristics such as biodegradability, thermal stability and non-toxicity translate a high value-added material for use in drugs. Despite these advantages, the mechanical strength of the material is still quite limited [79, 80].

3. Challenges

Even with promising trends for applicability, biodegradable polymers obtained from renewable sources present some disadvantages, such as low mechanical properties, rapid degradation rate, high hydrophilic capacity, and in some cases, poor mechanical properties, especially in humid environments, rendering their application unviable [81, 82].

In this context divergent opinions arise about the acceptability of biodegradable polymers in industry. While some believe in their potential to replace petroleum polymers, others presume that their shortcomings, both in technical and economic aspects, hinder their rapid adoption, at least in the near future [83].

The challenge is to obtain materials with properties equivalent to synthetic products [45]. To achieve this objective, different techniques are studied to promote modifications of biodegradable polymers, as shown in **Table 3**.

Author	Material studied	Aim of the study/Results obtained
[84]	Cellulose	Evaluation of the mechanical barrier, and interfacial properties of Methylcellulose (MC) films reinforced Poly (caprolactone)-based biodegradable films. It was found that MC film contributed to the improvement of mechanical properties of the composites. It was found that the methylcellulose film acted as a satisfactory reinforcing agent, contributing to the improvement of the mechanical and oxygen barrier properties of the composites for packaging applications.
[85]		Simultaneously achieve impact strength and bending properties (flexural strength and tensile strength) by improving the impact strength of modified cardanol (PAA) -bound cellulose diacetate (CDA) by adding flexible resins. In conclusion, the impact resistance of PAA-bound CDA was dramatically increased by the addition of a small amount of olefinic resins (polyethylene and polypropylene).

Author	Material studied	Aim of the study/Results obtained
[86]	Chitosan	Evaluation of the effects of adding the silicone liquid rubber to formulations of chitosan and alginate membranes both with and without silver-containing antimicrobial agent, to improve the overall mechanical properties of the dressings. It found that membranes containing the silicone rubber had a more homogeneous appearance and adequate flexibility and adhesiveness, increasing in tensile strength, both with and without the antimicrobial agent. In addition, the membranes without the antimicrobial agent resulted in a decrease in absorption of all physiological solutions tested.
[87]	Chitosan and gelatin	Development chitosan/gelatin composite films embedded with various amounts of wool nanoparticles. In conclusion, it was found that incorporation of wool nanoparticles into chitosan/gelatin composite led to a reduction in swelling, moisture content, dissolution degree and degradation rate of the films. However, tensile strength and elongation at break decreased upon loading the films with wool nanoparticles.
[88]	Starch	Incorporation of saturated fatty acids in the development of films made of starch and the biodegradable synthetic polymer poly (butylene adipate-co-terephthalate) (PBAT), concluding that the incorporation of saturated fatty acids until 12 carbon atoms reduces the permeability to water vapor and improves the mechanical properties of films made of starch, glycerol, and PBAT produced by extrusion, contributing to the formation of a cohesive and homogeneous polymer matrix.
[89]		Investigation of polyol mixtures including glycerol as plasticizer and high molecular weight polyol such as xylitol, sorbitol and maltitol used to plasticize corn starch, it being understood that the extra addition of high molecular weight polyol together with glycerol favored an improvement of the thermal stability and mechanical strength of the starch composite.
[90]		Verification of the influence of starch oxidation with sodium periodate on the functionality of active films based on gelatin and starch, obtaining an improvement in the properties of strength and barrier to water vapor and oxygen, reducing the water absorption capacity.
[91]		Evaluation of the effect of irradiation on the physicochemical properties, rheological and in vitro digestibility of the Kithul starch (*Caryota urens*). Concluded that the irradiation decreased the pH, swelling index, amylose and moisture content of the starch, increasing the content of carboxylic acid, acidity and solubility.
[92]		Characterization of rice starch gels reinforced with enzymatically produced resistant starch, resulting in an increase in the gel strength of about 60%, while cohesion decreased and the elasticity remained stable.
[93, 94]	Gelatin	Crosslinking induced by the enzyme transglutaminase in gelatin films, evidencing improvements in the physical, chemical and mechanical properties of the films.
[95]	Casein and soybean	Development and characterization of novel meltable polymers and composites based on casein and soybean proteins. In addition to the investigation of the effect of inert (Al_2O_3) and bioactive (tricalcium phosphate) ceramic reinforcements on the mechanical performance, water absorption and bioactivity behavior of injection molded thermoplastics, aiming at biomedical applications. And concluding that thermoplastics developed on the basis of casein and soy protein present an adequate range of mechanical properties and degradation as well as a bioactive character (especially when reinforced with bone-like ceramics) that may possibly allow its use as biomaterials in medicine.

Table 3.
Studies to improve the properties of biopolymers.

4. Conclusions

This chapter addressed a theoretical review of the opportunities and challenges of biopolymers, considering aspects such as generation and use of waste, sustainability and properties that make their applicability unfeasible.

In addition, it is necessary to continue the studies aimed at improving the poor properties of biopolymers, in order to contribute directly to scientific knowledge, ensuring sustainability, environmental preservation and consequently future generations.

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