Biopolymers to mitigate the environmental impact

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Polymers, commonly named plastics, are materials composed of long and repetitive chains of molecules with characteristic properties of the type of molecules and the bonds between them. They play an essential role in everyday life and are necessary materials for many specific uses, in particular it can be mentioned, for example, the food industry field. The main advantages of polymers are their low weight, good resistance to chemicals and the environment, flexibility and the possibility of made composite materials with improved properties. For example, a typical soft drink bottle of 1.5 liters made of Polyethylene terephthalate (PET) weighs around 50 g, while one made of glass weighs about 500 g, ten times more than the first!

There are many advantages and current uses of polymers, however, there are some disadvantages that should be considered. In particular, the massive use of polymers produces a large volume of waste that, due to its volatility and resistance, imply an impact on the environment. In the year 2017, the production of plastics in the world reached almost 350 million tons, of which 40 % is used for packaging [1]. According to data of industrial use sector from 1950 to 2015, the cumulative plastic waste generation will have been grown in an accelerated way to 2050 [2]. From these predictions, the waste discarded in landfills or the natural environment will slow down its growth reaching about 12000 million tons to 2050, while the incinerated and recycled waste will increase its growth reaching 12000 and 9000 million tons, respectively to 2050.

To understand what happens with polymeric materials after they have reached their useful life and are discarded, we will briefly refer to how are the degradation processes of this type of materials:

Polymer degradation

Degradation of a material means all types of transformations that affect its original composition and have an impact on its initial properties and benefits. These changes occur under the influence of one or several environmental factors such as heat, light, or some chemical agent as acids, alkalis or some salts. It is important to note that degradation is not equivalent to deterioration since the latter is a disintegration due to physical causes. It does not significantly affect either molecular weight or polydispersion.

In polymers, there are different types of degradation according to their chemical composition and the extrinsic factors [3]:

- **Thermodegradation** is a process by which polymers undergo chemical changes in their structure due to high temperatures that are applied to the material. It is based on the rupture of the covalent bonds or functional groups of the polymer causing changes in the glass transition temperature.
- **Photodegradation** is based on the physical and chemical changes that occur in the material due to the action of sunlight. As a result, the molecular chains are broken, reducing its molecular weight and mechanical properties.
- The **oxidative degradation** is a process that occurs in the presence of gases that are in the atmosphere, especially oxygen, which is activated on the polymer causing free radicals that induce secondary degradation reactions.
- During the fabrication and modification processes, polymers are submitted to tension and deformation, which produce **mechanical degradation**.
- The **chemical degradation** is produced when the polymer takes contact with chemical substances, like acids, bases and others.

- The **hydrolytic degradation** affects to the materials that are in presence of an aqueous media. The introduction of the water in the structure of the polymer produces the rupture of the intermolecular hydrogen bonds, hydration of the molecules and hydrolysis of unstable bonds.
- The **biodegradation** is produced by the action of microorganisms such as bacteria, fungi and algae to give CO_2, H_2O, mineral salts and new biomass in the presence of O_2 or CO_2, CH_4 and new biomass in the absence of O_2.

The most commonly used polymers are synthetic plastics, which are petroleum derivatives. Of these, the most used are: polyethylene, polypropylene, polyvinyl chloride, polyethylene terephthalate, polystyrene, polycarbonate and polymethylmethacrylate. The synthetic polymers in the long term, cause a problem of resources (they are manufactured with non-renewable resources and its synthesis requires appreciable amounts of energy) and a problem of elimination after their use. Their degradation enhances the greenhouse effect, as well as the effects of accumulation in ecosystems, where they play a serious threat to biodiversity and all kinds of wildlife. Polyethylene, polypropylene and polymethylmethacrylate are sensitive to oxidative degradation and UV radiation. On the other hand, polyvinyl chloride can discolor at high temperatures due to the loss of hydrogen chloride, thus becoming a brittle compound. Polyethylene terephthalate is sensitive to hydrolysis and attack by strong acids, while polycarbonate rapidly depolymerizes when exposed to strong alkalines.
In addition to the synthetic polymers, there are also the biopolymers, which are those from living beings. Within this category are the natural biopolymers such as DNA, proteins and polysaccharides that are fundamental to biological structure and function. It also includes those obtained from renewable sources, which are usually vegetables such as starch, corn or soybean oil, although there are also others of bacterial origin. These last biopolymers can be obtained from agricultural waste such as sugar cane, which is of great importance due to most of these wastes are generally burned or aerobically decomposed. The main advantage of the biopolymers is that they are obtained from renewable resources and the final pieces can mostly be considered as biodegradable either aerobically or anaerobically. This feature makes biopolymers a good alternative to solve the problem of contamination with respect to polymers. The disadvantages are their

high fabrication costs and the fact that they do not exhibit yet the mechanical properties that have the synthetic polymers. However, both limitations can be improved by means of serious investigations and efforts in relation to these promissory materials.

Biodegradation

To understand the advantages of biopolymers and green composites in the attempt to obtain more environmental friendly materials for use in daily life, a short explanation about the meaning of the biodegradation processes will be given below:

The biodegradation process is defined as a decomposition of materials by the action of microorganisms. However, it includes several steps [4]:

- The **biodeterioration**, which is the fragmentation of biodegradable materials by the combined action of microbial communities and other decomposing organisms.
- During the **depolymerization**, the molecular weight of polymers is progressively reduced by enzymes and free radicals secreted by the microorganisms. It generates oligomers, dimers and monomers. Some molecules can cross the plasma membrane, while others remain in the extracellular environment.
- During the **assimilation**, the molecules in the cytoplasm integrate microbial metabolism to produce energy, new biomass, storage vesicles and many primary and secondary metabolites. Some metabolites can be excreted and reach the extracellular environment.
- During **mineralization**, simple molecules such as CO_2, N_2, CH_4, H_2O and different salts of intracellular metabolites that are completely oxidized are released in the environment.

Biodegradation can be produced in different environmental conditions, such as soil, compost, marine environment and other aquatic environments. Terrestrial environments contain a great biodiversity of microorganisms, which allow the biodegradation to be more feasible with respect to other environments, such as water or air. Composting is a process in which organic matter is converted into CO_2 and humus by the activity of a mixed group of microorganisms. According to the American Society for Testing and Materials (ASTM), a compostable polymer undergoes degradation by biological processes during composting to produce

CO_2, water, inorganic compounds and biomass at a rate comparable to compostable materials, leaving no toxic residues [5]. In general, biopolymers are susceptible to biodegradation by compost. The biopolymers synthesized from biomass have the advantage that they can also be used as a substrate by microorganisms.

The biodegradation of the biopolymers is affected by the environmental characteristics and the chemical structure of the material. For example, polymers with a short chain, more amorphous zone and simple formula are generally more susceptible to biodegradation [4]. The crystallinity, molecular weight and the copolymer composition (for a copolymer) should also be considered [5]. It has been found that the reduction of the crystallinity of polyhydroxyalkanoates improve their biodegradability. The environmental factors also affect the biodegradation process, such as the temperature, moisture, acidity, oxygen presence (aerobic or anaerobic conditions) and pH [4, 5]. A low soil pH can deteriorate the microbial activity, leading to a slower degradation.

A recent study on the biodegradation of polylactic acid (PLA) under home composting conditions has shown that the biodegradation is very slow after 11 months [4]. It was related to the low temperature of the system in real conditions, due to these bioplastics need higher temperatures and longer times to be effectively degraded. However, the PLA/corn, PLA/sisal fiber and PLA/poultry feather fibers composites exhibited a high biodegradability. The same behavior is observed in PHA/rice husk composites, where the presence of rice husk increases the biodegradability properties [4].

In the marine system, plastic wastes can degrade into smaller particles, calls ***microplastics***, which contribute to the marine pollution and have a great impact on marine life. The presence of sediment, the temperature and the microorganisms that exist in the water also play an important role in biodegradation in aquatic systems. However, the plastic wastes are largely accumulated and exhibit an almost permanent stability. Therefore, the use of biodegradable polymers can also contribute to maintain a sustainable environment and protect the marine and aquatic system [4].

Examples of biopolymers obtained from biomass

Within the bioplastics globally produced in 2018, approximately 43 % are plastics with the ability of biodegradation [6]. This type of plastics are the focus of this work. The most produced biodegradable bioplastics are the starch blends and PLA. Polyhydroxyalkanoate (PHA) is less produced but has a low CO_2 emission [7]. It is worth mentioning that, from 2.11 millions of tons of bioplastics produced in the world, 9 % corresponds to South America [6]. Although this participation is low compared with Asia (55 %), the great agricultural activity in South America could convert this area in a development source. An example is the production of polyhydroxybutyrate (PHB) in Brazil [8].

Thermoplastic starch is a biopolymer that has received attention since decades ago as a material for different uses. Starch is totally biodegradable, but has poor mechanical properties, so it must be physically or chemically modified [9]. In this sense, blending with other biodegradable polymers, for example PHB [10], is an active research area. Other advantages of the starch is its low cost. Starch is composed of linear amylose and branched amylopectin (Figure 1).

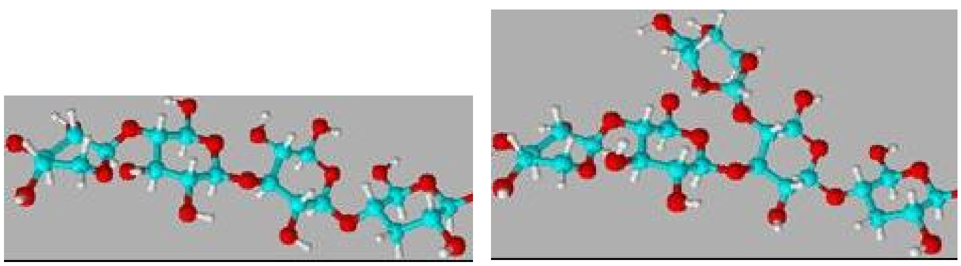

Figure 1. Left: structure of amylose and right: structure of amylopectin. (Color code: blue=carbon, white=hydrogen, red=oxygen)

In the gelatinization process by mixing starch powder, water and plasticizers, usually glycerol, the thermoplastic starch is obtained. In general, the starch could have potential applications in packaging materials for food if the mechanical and barrier properties are improved [11]. The machinery necessary to the processing of starch is similar to those used in other polymers. Besides, the thermoplastic starch is sensitive to moisture and temperature, as can be determined by dielectric spectroscopy. In Figure 2, a film of starch using as plasticizer glycerol in a solution of acetic acid 3% V/V is shown. The relation starch/glycerol is 50/50 in weight. The advantage of use a dilute solution of acetic acid is the low environmental impact compared with other acid solutions. The dielectric capacity (*C*) was determined in these samples as a function of the temperature before and after a thermal treatment of 2 h at 58°C. The obtained values are presented in Figure 3. It can be observed an increment of the value (*C* (Temperature) – *C* (Room Temperature))/ *C* (Room Temperature) as a function of temperature in both cases. This behavior suggests a marked sensitivity of this material with the temperature and water content.

Figure 2: Film of starch made with glycerol and a solution of acetic acid 3% V/V.

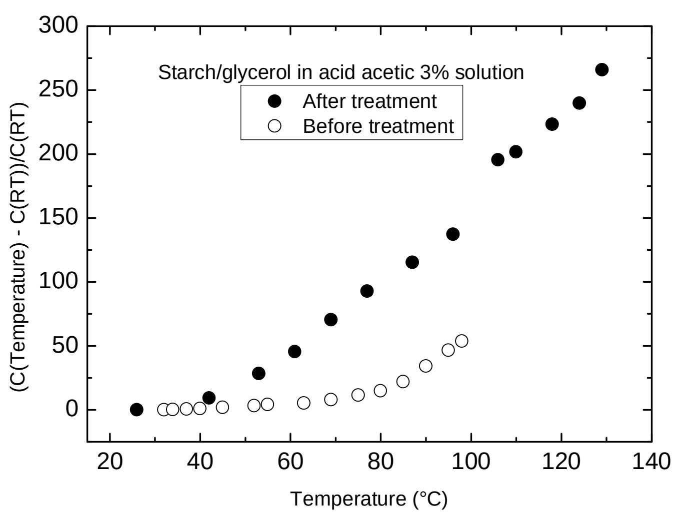

Figure 3. Dielectric capacity as a function of the temperature for starch/glycerol 50/50 in acid acetic 3% solution, before and after the thermal treatment of 2 h at 58°C.

As mentioned above, **polylactic acid** (PLA) is a biodegradable polymer, which is derived from lactic acid. Its structure is shown in Figure 4. The basic and most used obtaining process of lactic acid consists in the fermentation of carbohydrates with bacteria. Some of the most used substrates are: sugarcane and sugar beet sucrose, lactose from whey and dextrose from hydrolyzed starches. This biopolymer can be also obtained by bacterial fermentation from starch or agricultural wastes rich in starch. The obtained material is flexible, easily moldable, resistant and with a good moisture barrier. It is already used for dishes and disposable utensils and to pack food and drinks. PLA exhibits properties similar to polyethylene, so, it can be also used for non-alcoholic drinks and other non-food products. Depending on the manufacturing process, PLA can be also produced with different mechanical properties, to be rigid or flexible and may be copolymerized with other materials. On the other hand, PLA is one of the most used polymers for 3D printing.

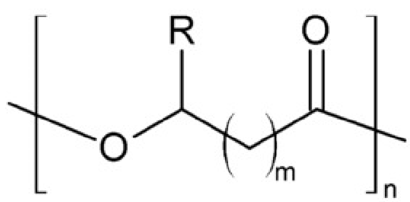

Figure 4. Structure of PHB: (R=methyl; m=1); PHV: (R=ethyl; m=1) and PLA (R=methyl; m=0) [5, 12].

Within the biopolymers, a group of materials with very promising properties corresponds to the **Polyhydroxyalkanoates** (PHA), which are linear polyesters biosynthesized by bacteria by means of the fermentation of sugars or lipids. Some bacteria, like *Shaeroides Rhodobacter*, produce those polymers and accumulate them intracellular as reserve material. Under conditions limited in essential nutrients (N, P, O, S or Mg), but with excess of carbon, microorganisms synthesize PHAs, which are deposited in the form of granules in the cells [13]. The PHA granules are then recovered by disrupting the cells. The obtained biopolymer exhibits good physical and mechanical properties, representing a favorable alternative to synthetic polymers, due to they are completely biodegradable and are also produced from renewable carbon sources. In addition to the biodegradability, the PHA have thermoplastic properties and a good moisture barrier capacity, resembling in part to polypropylene in its mechanical properties. However, it is more brittle, which limits, in addition to the high production costs, its massive application in food packaging.

There are many types of polyhydroxyalkanoates, but the best known are polyhydroxybutyrate (PHB) and poly-3-hydroxyvalerate (PHV), as well as their copolymers (see Figure 4). The first one, PHB, is the best known and the most widely used in food packaging.

Improvement of the mechanical properties of biopolymers

Recent studies are focused on improving the mechanical properties of PHAs, because their main disadvantage is the fragility as a pure homopolymer, associated with its high degree of crystallinity [14]. For example, a PHB/PHV copolymer is commercially available, obtaining an improvement in melt-processability and a better balance of stiffness and toughness for contents of 5-20 % of PHV [15]. This copolymer is less crystalline, more flexible and easier to process, and its properties can be easily modified by varying the valerate content [13]. This material is actually used for biodegradable containers, like shampoo bottles, or for example, disposable razors. Some researchers have focus on blends of PHB with other biodegradable polymers, such as PLA [16], starch [17, 18] and mixtures of PHB/PHV with maize starch [19]. Those examples could result in a completely biodegradable material with good mechanical properties, similar to the synthetic polymers, and with lower costs respect to pure PHB. With the aim of reducing production costs and make these materials more competitive, other attempts have been made on the production of PHA in transgenic plants with successful early results [13].

Other efforts have been made on the fabrication of composites of a polymer matrix with natural fibers. In some applications, like civil engineering, the challenge is find more environmental friendly processes and materials with competitive properties respect to the traditional building materials. In this field, the application of natural fiber/polymer composites is mainly concentrated on non-load bearings and for indoor uses [20]. To improve the behavior of this composites to environmental attack, several studies have been made about the use of different additives and treatments on the fibers, such as UV stabilizers or fire retardants [20]. The most used natural fibers are those obtained from plants, like wood, bamboo, jute, wheat straw, coir fiber, flax and best fibers, and those obtained from animals, which are composed of proteins from hair, silk or wool [13, 20, 21].

At this point, the dilemma between wanting a durable material during their use, but with biodegradable properties at the end of their useful life arises [4]. For example, in composites containing fibers, they exhibit good mechanical properties for indoor uses, but the action of the sunlight degrades the material.

The composites fabricated from biopolymers and natural fibers are commonly referred in the literature as “green composites”. Singh et al. [22] studied the improvement of the mechanical properties of the polyhydroxybutyrate-co-valerate (PHBV) with wood fiber composite for contents between 10 to 40 wt.% of fiber. Other authors have studied composites of PHBV with bamboo pulp, coir, wheat straw, cellulose, jute and abaca fiber and found excellent results on improvement the mechanical properties of the material [23-26]. An additional benefit of using natural fibers for composite materials is that they can be obtained from common agricultural and industrial solid wastes.

Final remarks

The aim of this work was to show some possible solutions to the environmental pollution due to the plastic problem. The strategy was to present some alternatives that, to our understanding, are more likely to be applied in a near future. The use of biodegradable polymers coming from natural sources or agricultural waste was developed by means of three examples: starch, PLA and PHA. On the other hand, the possibility of fabricate green polymers was briefly developed. PLA exhibits the greatest current development, while starch has the advantage of its low cost. PHA, mainly PHB, has good chances of replacing some synthetic polymers if its mechanical properties are improved.

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