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Biodegradable polymers: a review about biodegradation and its implications and applications

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Abstract

Plastic waste pollution is a global environmental problem that could be solved by biodegradable materials. In addition, its biodegradability has been important for medical applications. In this way, the biodegradability performance has been investigated for different materials under diversified environmental conditions. In this context, this review shows the main up-to-date biodegradable polymers (from renewable sources and fossil-based), their structure and properties, and their biodegradability characteristics. Also, this review shows the effect of polymer properties and environmental conditions on biodegradability, methods of biodegradability and toxicity determination, modification processes to enhance biodegradability, and main applications of biodegradable polymers for agricultural, medical, and packaging. Finally, this review shows a discussion about the implications of biodegradation on the environment, the current context and future perspectives of plastic biodegradation.

***Keywords*:** plastic waste pollution, biodegradability determination, composable, applications of biodegradable materials, plastic toxicity.

1 Introduction

Currently, people are progressively more aware of the need to exert environmental protection; therefore, academic research on environmental issues has received greater care[1]. Biodegradable polymers derived from renewable resources have gained great attention due to their desirable biocompatibility, biodegradability, and abundance[2]. Starch and fibers extracted from plant fibers are the most employed[3].

The biodegradation mechanism corresponds to microorganisms converting biochemical substances into compounds[4] and can be represented schematically in the four stages shown in Figure 1.

Based on Figure 1, in Stage 1 we can observe that the formation of a microbial biofilm leads to a superficial degradation in which the polymeric material is fragmented into smaller particles. This process depends not only on microorganisms' abilities but also on the properties of the plastic, such as topography, roughness, free energy, hydrophobicity, and the electrostatic interactions of their surface[5]. Then, biofilm microorganisms secrete extracellular enzymes, which catalyze polymer chains into oligomers, dimers, or monomers (Stage 2). The enzymes secreted by microorganisms for the biodegradation of materials are mainly lipase, K proteinase, and dehydrogenase[6]. The uptake of the small molecules produced in this way into the microbial cell and the subsequent production of primary and secondary metabolites is a process known as assimilation (Stage 3). Finally, in Stage 4, the metabolites are mineralized, the microbes are in a starvation phase and mineralization affects the storage of polymers and metabolites formed in Stage 2. The latter phase can be very long-lasting[7]. In general, the end products of biodegradation are CO_2 and H_2O in aerobic systems (oxygen is used as an electron acceptor by bacteria), and CH_4, CO_2, H_2O and biomass in anaerobic systems (absence of oxygen by microorganisms)[8].

Degradability is not only an environmental matter; medical applications of biodegradable polymers have gained attention lately[2]. Moreover, the demand to create alternative biodegradable water-soluble polymers for products such as detergents and cosmetics has also gained an increasing value[9]. Therefore, the development of biodegradable polymer materials and the design of methods to enhance biodegradability have become a major objective in academia[1].

In this context, we present the up-to-date main biodegradable polymers, their structure, and properties, as well as the effect of polymer properties and environmental factors on their biodegradability. In addition, we show biodegradability and toxicity, a discussion of the biodegradation implications on the environment, and the current context and future perspectives of plastic biodegradation.

2 Biodegradable polymer classification

Biodegradable polymers can be categorized into different groups. Regarding their source, they can be immediately obtained from biomass (polysaccharides and proteins), synthesized from biomass (poly (lactic acid) –PLA), and achieved by microbial fermentation (e.g., poly(hydroxybutyrate) –PHB and poly (hydroxy alkanoates) –PHA). Biodegradable polymers could also be synthesized from petrochemicals (e.g., (polycaprolactone) –PCL, poly (butylene succinate-co-adipate) –PBSA and poly (glycolic acid) –PGA). In the next section, the main biodegradable polymers are described.

2.1 Biodegradable polymers from renewable sources

2.1.1 Polysaccharides

Starch is a well–known hydrocolloid polymer from vegetable sources, cheap and abundant. It is predominantly obtained from potatoes, corn, wheat, and rice, composed of amylose (poly-α-1,4-D-glucopyranoside), a linear and crystalline polymer, and amylopectin (poly-α-1,4-D-glucopyranoside and α-1,6-D-glucopyranoside), a branched and amorphous polymer[10]. The proportion of amylose and amylopectin varies depending on the source, producing materials with different properties and biodegradability[10]. The applications of starches are extensively explored in all fields. Starch degradation occurs by hydrolysis, in which the α-1.4 link is attacked by amylases, while glucosidases attack the α-1.6 link[10], and produce non-toxic substances[11].

Chitin is the second most abundant natural biopolymer. It is a linear copolymer of N-acetyl-glucosamine and N-glucosamine with β-1,4 linkage. Chitin is usually found in the shells of crabs, shrimp, crawfish, and insects[10]. Some modifications of chitin could result in new polymers. In fact, chitin is processed into chitosan by partial alkaline N-deacetylation[12]. Biodegradation in the human body, immunological, and antibacterial activity are some of its biological properties useful for medical applications[13,14]. Other industrial applications are cosmetics and wound dressing[10,12]. The mechanism of chitin degradation occurs exclusively by the hydrolysis of glycosidic bonds by chitinolytic organisms[15].

2.1.2 Proteins

Proteins can be obtained from plants and animals[16], due to their renewability and biodegradability, and protein-based materials are useful in several industrial applications. Compared to starch, the proteins are also sensitive to water[16]. Therefore, blending with biodegradable polyesters is the most successful method of using protein in packaging applications[16]. However, in the medical field, collagen is highlighted due to the rich protein constituent of connective animal tissues. This has different applications, such as drug delivery including hydrogels, microparticles, sponges, biomaterials[14], implants matrix, and stabilizers in vaccines[17].

Proteins are degraded by proteolytic enzymes, which, depending on their primary amino acid sequence, could be more or less susceptible to degradation[18]. Protein folding, that is, secondary and tertiary structures, may make some regions less accessible to proteolytic cleavage[18]. Thus, the degradation behavior depends on the protein, and also on the type of material[18].

2.1.3 Polyesters

Polyesters are attained by polymerization of monomeLrs through fermentation (semi-synthetic polymers) or produced by microorganisms, grown under different nutrients and environmental conditions[10]. These polymers are potentially useful for degradable packaging materials and in applications in medicine, pharmacology, and agriculture applications[1]. The production of biodegradable polyesters for biomedical applications has improved significantly.

Polyester degradation is influenced by some factors, for example, pH, change in redox potential, and/or the presence of certain enzymes[19]. These polyesters could be hydrolyzed to obtain oligomers and then monomers[1]. Based on the types of monomers present in their raw material, polyesters can be aliphatic, aromatic, or copolyesters[20]. Aliphatic polyesters, such as polyglycolide (PGA), PLAs, polycaprolactone (PCL), or PHAs, have linear chain structures, low mechanical properties, and are easily biodegradable[20,21]. Aromatic polyesters, such as poly(butylene terephthalate) (PBT), have increased mechanical properties, but low biodegradability[20,21]. Although copolyesters have properties of both classes, enhanced physical and thermal characteristics, and biodegradability[20], the degradation rate is affected by the porosity of the polymer, crystallinity, and pH of the solution[1]. Commonly, low crystallinity and high porosity both accelerate the degradation ratio. In comparison to compost, the degradation in soil and liquid media is lower, mainly due to the lower temperature[22].

PLA is produced from lactic acid via starch fermentation of lactic bacteria[10], which gained attention due to its availability, cheapness [23], biodegradability, and biocompatibility[21,24]. PLA is used mainly for general packaging applications, thanks to its processability through common thermoplastic technologies[21]. Furthermore, PLA nanomaterial has been used extensively for numerous biomedical applications, e.g., drug delivery, nanocarriers to encapsulate water-insoluble drugs in the circulating blood, etc[24].

Regarding biodegradation, several studies showed that PLA is completely degraded under compost conditions[10].

PHA is another material applied in many sectors, which is a polyester of various hydroxy alkanoates that is synthesized by microbial fermentation. PHAs application is restricted due to their reduced mechanical properties, incompatibility with conventional thermal processing techniques, and relative higher thermal degradation[23]. However, they are entirely biodegradable which occurs via linkage break by esterases of the monomer from the chain ends[10]. PHB is the most popular of the PHAs with a high degree of crystallinity. It has the advantage of biodegradability by the action of PHA hydrolases and PHA depolymerase forming (*R*)- and (*S*)-hydroxybutyrates and non-toxic compounds under aerobic and anaerobic conditions[23]. Another copolymer is hydroxybutyrate and hydroxy valerate (PHBV), which showed a degradation rate faster than the PHB, in which the degradation kinetics hang on the structure, the crystallinity, and the processing conditions[10].

2.2 Biodegradable polymers from fossil-based polymers

Fossil fuel-based biodegradable polymers such as poly (butylene succinate-co-adipate) (PBSA), poly (butylene succinate) (PBS), polycaprolactone (PCL), and poly(butylene adipate-co-terephthalate) (PBAT) have some advantages that could be used in many industrial fields, not only for plastic production[16].

2.2.1 Polycaprolactone (PCL)

PCL is a semicrystalline aliphatic polyester produced by ring-opening polymerization of ε-caprolactone in the presence of various anionic and cationic catalysts[1]. It is suitable for the production of prolonged-release delivery systems due to its slow biodegradation[1]. However, despite reduced degradation rate, easy accessibility, and good mechanical properties, applications have been limited due to their high cost[1]. The degradation takes place in two stages; first, the hydrolytic cleavage of the ester bond and then the intracellular degradation into the nontoxic metabolites that are excreted directly from the body or after the metabolic change in the Krebs cycle[1]. Recent studies showed that PCL microplastics were found in the Mediterranean sea providing evidence that PCL does not easily degrade under natural conditions[25], reinforcing its limitations.

2.2.2 Poly (butylene succinate) (PBS)

PBS is synthesized by the polycondensation reaction between succinic acid and butanediol[26], with good thermal stability and mechanical properties[26]. The applications of PBS are expanding in many areas, such as packaging, mulching films for agriculture, or delayed-release materials for fertilizers and pesticides[26]. PBS has a low relative biodegradation rate due to its high crystallinity and it decomposes into nontoxic and harmless products, such as water and CO_2[26]. To increase biodegradability, several approaches have been used, such as physical blending, copolymerization, or composite formation[26]. Some studies showed that PBS could be degraded by enzymatic attack in the amorphous and crystalline structure[27]; it was observed by Fourier Transform Infrared Spectroscopy (FTIR) that the main chain scission was at the ester linkage[27].

2.2.3 Poly (butylene adipate-coterephthalate) (PBAT)

PBAT is synthesized from 1.4-butanediol, terephthalic acid, and adipic acid monomers by polycondensation reactions, and has mechanical properties analogous to the low-density polyethylene (LDPE), while the oxygen barrier property is 50 % lower than LDPE[16]. PBAT is an attractive material for agricultural mulch films and food packaging[16]. The degradation is affected by microorganisms that excrete enzymes into the environment, attack the polymer surface and cleave polymer chains[22]. Although microorganisms are fundamental for the entire degradation mechanism, they can also be abiotic, which is a step that precedes the assimilation governed by chemical, thermal, mechanical and photo degradation[22]. Small oligomers and monomers formed during biodegradation are digested by microorganisms producing CO_2, H_2O, and CH_4[22].

3 Effect of polymer properties and environmental factors on biodegradation

It should be noted that several factors affect the biodegradation process, such as the properties of the polymers (molecular weight, shape and size, type of functional groups, crystallinity, and exposure conditions (temperature, humidity, pH, and current microorganisms).

The chemical structure of a polymer is the main factor determining whether the polymer can or cannot biodegrade and how to achieve it[28]. Crystallinity is the property that limits the accessibility of water to the polymer chain, whereas amorphous regions are more flexible and accessible, thus being more susceptible to both hydrolysis and biodegradation than crystalline regions[28]. Also, the dimensions of the material are critical for biodegradability. Ruggero[29] evaluated the importance of the thickness (ranging from 50 and 500 µm) of a PLA film in the biodegradation process. Only 3 % of the film content with 500 µm of thickness degraded when conditioned in thermophilic conditions (0 days: 58 °C and 50-55

% of relative humidity, 40 days: 37 °C and 50-55 %), although 50-μm thick films had total biodegradation after 2 months under these conditions.

With respect to environmental factors, soil moisture and temperature play an important role in the growth of microorganisms. As moisture increases, there is an increase in the hydrolytic cleavage of microorganisms, and the degradation capacity of enzymes decreases when the optimum temperature. Thus, polymers with a high melting point are less likely to be degraded. Another factor is pH, as it affects the speed of the hydrolytic reaction and the rate of microbial growth, and therefore, the rate of degradation[30]. We can also cite oxygen supply and light as being crucial factors in the degradation rate since these factors vary depending on the environment. For example, in composting plants, the temperature can reach 50-70 °C, and in the Arctic Ocean, it can be around the freezing point[31]. Another example is that soils can show diversified pHs; Mergaert[32] studied the degradation of PHBV (poly(3-hydroxybutyrate-co-3-hydroxy valerate) in soils with pH values between 3.5 and 7.1 and noticed that the polymer degraded more rapidly at lower pH values. Therefore, note that the same polymer can present different rates of biodegradation in different environments. Therefore, it is crucial to assess the sustainability of use and ensure a suitable degradation profile for the intended application or use in waste management.

Another crucial factor for biodegradation is the viable count of microorganisms, as the values differ significantly in different environments. For example, in compost, there are 10^7-10^8 colony-forming units per gram of material; in soil, 10^6 colony-forming units per gram of material[31]. However, it is not just the total count of microorganisms that matters, but also its ability to degrade any polymeric substrate. PCL biodegradation was evaluated in freshwater (lake and river) and seawater (bay and ocean), and the authors noted different degradation rates depending on the environment, due to the differentiated presence of degrading microorganisms[33]. These authors determined the following sequence of degradation rates: seawater (bay) > freshwater (river) > freshwater (lake) > seawater (ocean). For example, *Rhizopus arrhizus, Rhizopus delmar, Candida cylindracea,* and *Achromobacter sp*. are fungi that produce enzymes such as esterases and lipases which have shown degradation capacity on complex polymers such as PCL (poly(caprolactone)) and PEA (poly(ethylene adipate))[34]. PHB (poly(hydroxybutyrate)) can be degraded by gram-negative and gram-positive bacteria such as *Streptomyces* and *fungi*. PBS (poly(butylene succinate)) can be degraded by 39 bacterial strains of *Firmicutes* and *Proteobacteria*[31].

There is a specific class of biodegradable material called compostable that shows degradation undergone by biological processes during composting to produce CO_2, inorganic compounds, water, and biomass at a rate consistent with other known compostable materials and leave no visible, distinguishable, or toxic residues[35]. Thus, compostable plastic is biodegradable, while biodegradable material is not always compostable; marking all biopolymer-based packaging under the tag “eco-friendly”, “sustainable” etc. is not the complete truth, because they require specific conditions[36]. Environmental concerns and regulations adopted in different regions of the world make composting an increasingly attractive route for polymer disposal. However, compostable plastics do not completely decompose on their own, as in garbage or marine environments, because they need special conditions to favor their degradation. Compostable plastics must be composted in commercial facilities that have the equipment to shred and compost the material, which can take up to 180 days to decompose[37]. Therefore, the term "biodegradable" or “compostable” should include detailed information about the environment tested and associated data.

4 Methods of biodegradability determination

The biodegradability of plastic materials conventionally is first assayed using laboratory and simulation tests, where the conditions can be better defined and controlled. However, biodegradability should also be studied under real conditions (field) to know the correct impact on the environment. Figure 2 shows the aim tests used to determine the biodegradability of solid polymers.

In laboratory tests, enzymes and cell cultures are used to create an artificial environment to determine the biodegradability of plastic. To translate the results of enzymatic degradation conducted in the laboratory into biodegradation *in nature*, the microorganisms used must also be present in the environment where plastic can be found. Therefore, the use of current microorganisms is an important factor in evaluating the biodegradability of a particular polymer in a real-world environment. Eubeler[38] evaluated PLA degradation of PLA using the standardized test D5247-92 for the aerobic biodegradability of plastics with specific soil-dwelling microorganisms *Treptomycessetonii* and *Streptomycesviridosporus* in culture media. These microorganisms were able to degrade PLA; however, the tests conducted were limited to these specific microorganisms, because the PLA polymer was the only carbon source for these microorganisms. In a natural environment, this polymer may not be the preferred substrate, since other alternative nutrients available.

In this context, microorganisms may not be prevalent in the complex biota mix in the environment in question, and their ability to survive, compete, and thrive in that specific environment is critical. Therefore, most standardized biodegradation tests from the Organization for Economic Co-operation and Development (OECD), International Organization for Standardization (ISO), and American Society for Testing and Materials (ASTM) mandate the use of simulated or real environments to allow for a more realistic assessment. These standard tests determine biodegradability, as well as the degree or rate of degradation. The standards also form the basis for the certification of materials as compostable and biodegradable. In general, these standards define deadlines, test guidelines, procedures, limits, conditions, and interpretation of results[23]. In the following, we briefly describe the methods that have been most widely used to determine the biodegradability of solid polymers.

For the determination of biodegradability, one of the most important parameters is the carbon dioxide release caused by the consumption of polymeric materials by microorganisms. Other low molecular weight metabolites such as alcohols, aldehydes, methane, and fatty acids, among others, can be tested by gas chromatography with mass spectrometry[39]. Finally, residual polymers and their oligomers have been analyzed by gel permeation chromatography (GPC) to monitor changes in molecular weight and distribution[40].

4.1 OECD Biodegradability Tests

The OECD 301 series (OECD 301A – F) provides direct certification of the biodegradability of material, setting limits for the classification and commercialization of materials under the concept of final or ready biodegradability[41]. The readily biodegradable material shows 60 - 70 % of organic carbon converted to CO_2 within a 10-day window. However, the final biodegradable material (inherent biodegradability) shows 60 - 70 % of organic carbon converted to CO_2 over a total of 28 days. OECD 311 has been frequently most applied to assess the biodegradability of organic chemicals under anaerobic digester conditions. In the case of solid polymers, this method is used to evaluate their biodegradation if it occurs in an anaerobic digester.

4.2 ASTM Biodegradability Tests

The standard method ASTM D5210 (2007) consists of a *"Standard test method for determining the anaerobic biodegradation of plastic materials in the presence of municipal wastewater sludge"*. It has been used to evaluate the biodegradability of plastic materials under anaerobic conditions (a biological reactor is normally used to digest sludge after water treatment). This is interesting information since plastic solids that may not have been degraded under standard aerobic conditions often end up in anaerobic digesters as the last treatment option before being discharged into the environment.

The ASTM D5338 (2011) standard method consists of a "*Standard test method for determining aerobic biodegradation of plastic materials under controlled composting conditions, incorporating thermophilic temperatures*". It determines the biodegradation of plastic materials under optimal composting conditions (temperature, oxygen, pH, and humidity). This is a very relevant test, as there are commercial composting facilities that are based on these assessments. The testing can take up to 180 days and there are no limits or biodegradability ratings presented for certification purposes. The standard method ASTM D5988 (*"Standard test method for determining aerobic biodegradation of plastic materials in soil"*) (2012) is complementary to the ASTM D5338 method in that it also evaluates the biodegradability of solid polymers under aerobic conditions in the soil, but of residual material not degraded in the period of ASTM D5338.

The ASTM D6400 test standard (2004) ("*Standard Specification For Compostable Plastics*") evaluates the criteria for specifying the material as being "compostable". The criteria are related to disintegration, biodegradation, and ecological impacts. This method also analyzes heavy metals to ensure that the material is within the standard limits for healthy composting. Disintegration and biodegradation tests are carried out simultaneously. Disintegration has been evaluated by sieving the compost-plastic mixture for a set time to measure the amount of plastic passing through the sieve. Biodegradation consists of a measure of converting organic carbon to CO_2 under thermophilic and aerobic composting conditions. ASTM D5338 corresponds to the method used to assess biodegradation. Ecological impacts are assessed using OECD 208, which is a plant growth test. In this test, residual compost is mixed with the soil in specified proportions to assess the ability of standard plant types to thrive on compost residues. If all the evaluated criteria are met, the material can be classified as compostable.

In these tests, the samples are tested against a positive control material that already exhibits known composting behavior. The compostability of the samples is visually assessed at weekly intervals in conjunction with biowaste rotation, and the weight loss is measured at the end of the test when the positive control sample is fully degraded[45].

In addition to these ASTM methodologies, several other ASTM standards for assessing biodegradability have been included and updated in the last two decades (D5988-12, D6340–98, D6691–09, D5511–12, D5526–12, D5929–96 (2009), D6691–09, D6954–04 (2013)).

4.3 ISO Biodegradability Tests

ISO methods are presented according to test environment types (e.g., inoculum, compost soil) and measurement analysis (e.g. gravimetric, respirometry) without involving microbial strains[46]. Specifically, the ISO 14855 evaluates the biodegradability of solid polymers under aerobic conditions in an aqueous media and the inoculum sources for the test vary according to the final disposal (e.g., soil, compost, or sewage sludge). The percentage of organic carbon converted to CO_2 represents biodegradation. This test has been run for 6 months and does not allow explicit limits or ratings for certification purposes.

Using sewage sludge found in effluent treatment plants, ISO 9439 assesses the aerobic biodegradability of organic compounds in aqueous media. This method resembles the OECD 301B method setup. The ISO 14593 method assesses biodegradability under the same test conditions, but the test is performed in sealed containers similar to OECD 310. For both ISO methods, the percentage of organic carbon converted to CO_2 represents biodegradation. The trial duration is 28 days and these tests do not allow explicit limits or ratings for certification purposes.

The ISO 14855 methods assess the aerobic biodegradability of plastic materials under controlled composting conditions (temperature, oxygen and moisture, pH). This method is similar to ASTM D5338 standard method, and biodegradation is measured as the percentage of organic carbon converted to CO_2. The trial lasts 180 days, and this test does not allow explicit limits or ratings for certification purposes. The method is the preferred test for polymeric packaging materials under aerobic conditions because it provides an easy comparison as an international standard[45]. Finally, ISO also provides a standard procedure for describing sample preparation in DIS 10210[46].

As shown, different standards for biodegradability of plastics (for example, OECD, ASTM, and ISO) have different composting conditions, which prevents the comparison of results. Therefore, to encourage the development of these materials, an international consumer-recognized logo indicating that the material purchased is compostable is needed[47]. Despite the existence of many methods to evaluate the biodegradability of plastics, comprehensive comparative analyzes of these methods are still lacking in the literature to better inform their merits and shortcomings. Furthermore, these methods typically only require 180 days, while actual polymer degradation can take years to complete. Another critical factor is that there are many different metabolic pathways, along with many different biodegradation mechanisms, resulting in a variety of test methods (e.g., static, continuous, semi-continuous, aerobic, anaerobic, marine, and aquatic systems)[47].

5 Modification processes to enhance biodegradability

It is feasible to produce biodegradable polymers for a specific application; appropriate chemical modification improves biodegradability[2]. For example, the insertion of ‘weak links’ on non-biodegradable polymers could increase biodegradability[2]. Some methods have been established to improve the properties of biodegradable polymers, such as physical blending, grafting, or copolymerization. These methods improve both the performance of a specific property and the biodegradation rate. Therefore, in this section, some of the processes to enhance biodegradability are discussed.

5.1 Blend of polymers

Blending polymers is a method of reducing the overall cost and offers an alternative to modify both the properties and the degradability[2]. Due to starch properties, there has been growing interest in synthesizing starch-based products[23]. Starch-based thermoplastic is obtained by blending with polymers such as PLA, PHA, and PCL, which has received wider industrial applications, such as film blowing, extrusion applications, injection molding, blow molding, and foaming[23]. Blending must produce a fine enough dispersion so that the remaining thermoplastic part does not contaminate the environment after disintegration[2]. However, to achieve highly compostable materials, a higher amount of starch (up to 60 g/100 g) is required[23]. Nevertheless, at high starch content, the incompatibility of different polymers due to the different polar characteristics will affect mechanical properties[28]. Therefore, the balance between biodegradability and mechanical properties is still a challenge[23].

Another alternative to blending polymers is the introduction of the aromatic ring into a polyester structure (in the main chain or pendant to the backbone) to obtain biodegradable aliphatic/aromatic polyesters with much wider mechanical, thermal, and (bio)degradation properties[21]. In this case, the most important controlling parameter is the difference in temperature between the melting point of the materials and the degradation temperature[22], because the temperature controls the flexibility of the polymer chain and, thus, the mobility of the chains to fit the active sites of the enzyme[22]. Several studies have investigated blends to improve biodegradability, and some representative studies are shown in Table 1.

Table 1. Some representative studies concerning blends of polymers to increase biodegradability

Polymer blend	**Media**	**Degradation characteristic**	**Main Results**	**References**
Starch/PLA	Soil	Weight loss	The results showed that starch accelerated PLA degradation of PLA (70 days of soil degradation: the compound showed a weight loss of 15.94 % while PLA showed 0.15 %). The carbon content decreased, and the oxygen content increased by the hydrolysis of PLA.	48
PHBV/PBAT	Soil	Weight loss and surface characterization	PHBV substantially enhances the toughness properties of biocomposites and their biodegradability. 112 days of degradation in soil: PHBV showed weight loss of 0.5 % while PHBV/PBAT, 9 %.	49
PHBHHx/PBAT, PHBHHx/PLA, and PHBHHx/PBS	Seawater	The consumption of O_2 was evaluated using a BOD tester	Poly (3-hydroxybutyrate-co-3-hydroxyhexanoate) (PHBHHx) sheets showed good biodegradability, which was influenced by the weight ratio of the PBS. 28 days in seawater: PHBHHx increased the biodegradability of PBAT by 31 %, PLA by 34 %, and PBS by 51 %.	50

PCL/TPS	Compost and soil	Concentration of CO_2	The blend with 70 % of thermoplastic starch (TPS) and 30 % of poly (ε-caprolactone) demonstrated good biodegradation, with the initial rate almost equal to pure TPS in both environments (compost and soil). 90 days in soil conditions: PCL showed carbon mineralization of ~ 20 % while PCL/TPS (30/70) showed ~ 70 %.	51

5.2 Grafting

Grafting is a simple and efficient method to fine-tune the physical/chemical properties or functionality of materials[52]. A graft copolymer consists of a high-weight macromolecular chain of one monomer, referred to as the backbone polymer, with one or more branches or grafts of different monomers/polymers[13]. Regarding applications in the packaging field, the grafting of natural monomers such as cardanol, twelve hydroxy stearic acid, vanillic acid, etc. onto polyethylene can bring grafted polymers in which biodegradation can proceed easily[2]. In medical applications, grafting of tissue with known biodegradable polymers is expected to provide an improved ability to hold and release hydrophobic drugs, which allows delaying the material degradation time[53]. For example, graft-modified copolymers based on polysaccharides have improved water solubility, film formation ability, viscosity, thermal stability, rheological, and gelling characteristics[54]. After grafting, the crystallinity of the polymer could gradually decrease because the side chains are substituted randomly and the regularity in the chain is destroyed[13]; this increases biodegradability, as exposed previously. Representative studies on grafted polymers to enhance degradability are presented in Table 2.

Table 2. Representative studies on grafting modification to increase biodegradability.

Polymer	**Modification process**	**Media**	**Degradation characteristic**	**Main Results**	**References**
Cellulose	Graft copolymerization of cellulose with montmorillonite concentrations (3 to 9 g/100 g)	Soil	Cellulase activity	The biodegradability of grafted cellulose was increased by the addition of clay.	[55]
Xanthan gum	Grafted xanthan gum (XG) with poly (N-vinyl imidazole) (PVI)	-	Thermo degradation (TGA)	The TGA curve showed that its degradation rate was lower than that of pure XG.	[56]
Low-density polyethylene (LDPE)	Grafting highly hydrophilic monomers such as glucose to obtain 4-O-hydroxymethyl D-	Soil burial	Optical density	Results showed an increase in the degradation due to grafting.	[2].

	arabinose (Sugar) end-capped LDPE (Su-g-LDPE)				
Copolymers of gelatin and polymethyl methacrylate	Grafting of copolymers using the tributylboron–oxygen (TBB)	Aqueous suspension	Microbiological effect of some types of *fungi*	The results showed that the samples were biodegradable and, after the end of their service life, could be disposed of by soil *micromycetes.*	57
Poly DL-lactide (PLA), polyglycolide (PGA), and poly DL-lactide glycolide (PLGA)	Grafted copolymers	Porcine submucosa, ureter and bovine pericardial tissue	Pepsin and collagenase digestion assays	The results showed that biodegradability can be tailored by varying the type of grafted polymer.	53

PLA, PHB, PHBV, Bioflex (PLA blend), or Solanyl (starch-based).	Compatibilized with maleic anhydride (MA)	-	Photo-degradation	Degradation was evident through microcracks in all the samples, which led to higher water absorption.	58
Polypropylene films (PP)	Grafting	Compost	Quantifying the CO_2 (ASTM D5338-11)	The net cumulative CO_2 produced increased with the degree of grafting. The biodegradability of the cellulose was 76 % in 45 days.	59
Poly (propylene fumarate) (PPF) for 3D printing scaffolds	Grafting	-	In vitro degradation	The scaffolds produced showed adequate mechanical properties and were capable of supporting the growth of vascular tissue in	60

				vitro and *in vivo* due to the slow degradation rate.	
Cassava starch-g-polyacrylic acid/natural rubber/polyvinyl alcohol blends	Cassava starch grafted with polyacrylic acid	soil	Loss of weight	The products exhibited excellent water-retention capacity and a high extent of biodegradation.	61

5.3 Cold Plasma

Cold plasma treatment modifies the film surface and thus enhances the rate of microbial degradation, which is influenced by the treatment time, gas type, plasma power, electrode design and distance, structure, and components of the films[62]. The enhancement is possibly due to the development of chain ends and free volumes within the film network, thereby accelerating microbial biodegradation[62]. According to Hoque[63], the greater degradation due to the plasma-treated film is ascribed to the growth of the surface area that produces a porous structure and thus improves the availability of the microbes present in the degradation environment. Some representative studies are presented in Table 3.

Table 3. Representative studies concerning cold plasma treatment to increase biodegradability

Matrix	**Modification process**	**Media**	**Degradation method**	**Main Results**	**References**
PLA films	Cold plasma treatment	compost	Photo and thermal degradability	The results showed improved biodegradability of the PLA films, without negatively affecting the film properties.	62
30 % Corn starch/poly(ε-caprolactone) (CSPCL) 65 %; PCL and 5 % additives	Cold plasma treatment	soil burial	Mechanical properties over the period	Plasma enhanced adhesion and growth of microorganisms due to hydrophilic and rougher surface and thus, degradation.	64
Defatted soybean meal (DSM)-based edible film	Cold plasma treatment	Compost	Surface modification	Increased surface area may promote the biodegradability of the DSM-based film.	65

6 Main applications

Figure 3 presents the number of studies according to the *Web of Science* database involving biodegradable polymers and their applications from 2017 to 2021. The terms used in the research were: (TS=(polymer AND biodegradation AND medical application)) OR (TS=(polymer AND biodegradation AND tissue engineering)); (TS=(polymer AND biodegradation AND packaging)) OR (TS=(polymer AND biodegradation AND films)); (TS=(polymer AND biodegradation AND agricultural application)) OR (TS=(polymer AND biodegradation AND mulch film)); (TS=(polymer AND biodegradation AND automotive)); (TS=(polymer AND biodegradation AND electronics)); (TS=(polymer AND biodegradation AND construction)).

As shown in Figure 3A, > 60 % of the published articles involve the study of biodegradable polymers and their application in the packaging field, followed by medical and agricultural applications. This tendency of the application sector is maintained throughout the years as shown in Figure 3B, as already pointed out by several authors. The main agricultural, packaging, and medical applications are discussed as follows.

6.1 Agricultural

In agriculture, soil cover with plastic film has played an important role to improve grain harvesting yield and water use efficiency, because these films maintain the soil moisture, increase soil temperature, control weeds, and insects, minimize soil erosion and prevent soil splashing on fruits or vegetables[67].

Generally, plastic films consisting mainly of linear, low-density materials, such as low-density polyethylene, which are not readily biodegradable, are used for this purpose[68]. Thus, these covers need to be recovered and discarded after use. Additionally, recycling these materials presents difficulties, as these films are often contaminated with soil. To bring about more sustainable options, new promising formulations of biodegradable polymers have been developed in recent years.

Biodegradable materials applied to soil can be degraded by the action of soil organisms, saving disposal and labor costs. However, they must still meet the properties of conventional films by creating favorable microclimates for plant growth, flexibility for mechanical installation, maintaining integrity until harvest time, degrading after soil incorporation or composting, and not releasing toxic substances into the environment, and being cost-competitive[67].

Literature reported biodegradable materials capable of acting as mulch films, but the environmental consequences of the use of biodegradable materials have not yet been thoroughly studied, and international standards (ISO 17088, ASTM D6400, ISO 17556, ASTM D5988) to validate their security are not yet stringent enough[68]. Bio-based polymers made of cellulose, starch, polyhydroxyalkanoates (PHA), bio-polyethylene, and PLA are employed in the manufacturing of these mulching films and also shade nets[69]. The shade nets are vital in integrated pest management due to the toxicity of commercial pesticides—reducing pesticides has ecological and economic benefits and better mechanical properties compared to the traditional LDPE films[69].

Other example of agricultural application are biodegradable materials to produce tubes (containers used in the production of seedlings). There are already commercially available tubes of biodegradable seedlings, but they still do not meet the target dynamics of forest seedling production, as they have low mechanical strength, present cracks, and deformation of the tube structure, making handling difficult during application and transport to the field [70]. Several researchers have hence been trying to develop green materials based on biodegradable polymeric composites with a variety of lignocellulosic matrices, such as wood dust[71], and rice husk[70], among others.

Another example of application are agro-wastes derived from diverse sources including grape pomace, tomato pomace, pineapple, orange, and lemon peels, sugarcane bagasse, rice husks, wheat straw, and palm oil fibers, among others are available materials to the production of bio-based packaging[69]. In fact, the main applications of agricultural waste-derived biopolymers are in food packaging, which will be discussed in the next section.

6.2 Packaging

The number of materials used for packaging is growing continuously. If current consumption patterns and waste management practices do not improve by 2050, there will be about 12 billion tons of plastic litter[72]. Over the last few years, academia and industry have been looking for a suitable solution to environmental problems using biodegradable polymers to produce plastics. The development of biopolymer-based packaging is one such alternative to reduce the use of conventional plastic made from petrochemicals.

Biodegradable polymers can be processed by most common packaging processing techniques, with some modifications of processing conditions[10]. Some materials are already being introduced into the market e.g. *MaterBi* (Novamont S.p.A., Novara, Italy) *GSPla* (Mitsubishi Chemical Co., Tokyo, Japan), *Apexa* (DuPont, Wilmington, DE), *Ecoflex* (BASF), *Novon* (Warner-Lambert Co., MorrisPlains, NJ), *NatureWorks* (NatureWorks, Minnetonka, MN)[20].

Most conventional plastics are very resistant to degradation and persist for years in the environment. The American Society for Testing and Materials (ASTM) defines a degradable plastic that undergoes a significant change in its chemical structure under specific environmental conditions, resulting in a loss of properties measured by standard test methods and in a period that determines its classification[35]. Degradation can be promoted by abiotic (UV irradiation, heat, chemicals, photooxidative, thermal, ozone, catalytic, mechanochemical) and/or biological biodegradation processes[73]. In this context, the degradation of biodegradable materials is due to the action of naturally occurring microorganisms, such as bacteria, fungi, and algae[35]. Moreover, if degradation undergoes by a biological processes to yield CO_2, water, inorganic compounds, and biomass at a rate consistent with a known compostable materials and leave no visible, distinguishable or toxic residue, the material is known as compostable[74]. Thus, compostable plastic is biodegradable, while biodegradable plastic is not always compostable; marking all biopolymer-based packaging under the tag "eco-friendly", "sustainable" etc. is not the complete truth, because they require specific conditions[75] .

Biodegradable polymers and their blends have found applications in short lifespan service, as well as flexible and rigid packaging applications. Currently, Europe is leading the movement in advancing biodegradable packaging across the globe[16]. It can be seen that the future trend is to turn the flexible packaging market from non-biodegradable polymer material to biodegradable polymer materials[16]. However, various challenges remain for biodegradable polymers towards practical packaging applications. Particularly pertaining to the poor gas/moisture barrier issues which greatly limit the packaging[76].

Food-grade biopolymers such as starch, chitosan, methyl-cellulose, alginate, agar etc., have found application as packaging material in the food industry.[77] Also, perishable agricultural produce such as fruits and vegetables have been explored in the last decades[77]. Recent advances in the development of bio-based plastic have popularized their use as active/smart packaging systems for food commodities that enhance the product quality and shelf-life [77], mainly due to the presence of anti-microbial agents that has specific properties e.g. absorb ethylene, water vapor and thus, protect fruits, vegetables or other type of commodities from microbial contamination such as *Bacillus subtilis, Escherichia coli, and Listeria monocytogenes*[69]. For example PLA with Propolis ethanolic extract or Tanacetum balsamita essential oil extended shelf-life of sausages[78]; blends of PLA + Chitosan could inhibited microbial growth on pork meat [79]; blends of PVA + Chitosan inhibit *Bacillus subtilis, Escherichia coli* in minimally processed tomato[80] among several other studies reported in the literature.

6.3 Medical applications

The biopolymers used in medical applications must be biocompatible and they may or not be expected to break down after a given period[33]. Biomaterials play an increasingly important role in the repair of severe bone defects[81]. A scaffold made of biodegradable materials can provide a crawling bridge for new bone tissue that could eventually degrade and absorb in the body[81]. For example, for implantation, the scaffold must degrade promptly to ensure proper remodeling of the tissue[82]. Other applications include matrices for enzyme immobilization and controlled release, therapeutic devices, temporary prostheses, and porous structures for tissue engineering[10].

Proteins are the main components of different tissues and have thus been widely used for sutures, hemostatic agents, scaffolds, and drug delivery systems[10], because safe building blocks are useful in diverse pharmaceutical applications[18]. An example of protein is gelatin, which is used for coatings and microencapsulating various drugs[10].

In addition, microplastics (<5 mm) have been added to cosmetic products in search of different functions, such as exfoliation and skin cleansing (microspheres), opacity control, skin lightening, feeling of silkiness and smoothness, and viscosity control[83]. After use, these microspheres are poured down the drain and end up in Effluent Treatment Stations, where they can escape into the water. Once discarded, there is no efficient method of recovery and environmental conditions do not allow full biodegradation[84]. Polyethylene (PE) corresponds to 90% of microspheres in cosmetics, however, we can also find microspheres of polypropylene (PP), methyl methacrylate (PMMA), polystyrene (PS), and polyethylene terephthalate (PET)[85,86]. Given this, there is great pressure from the scientific community, non-governmental organizations and growing public concern to take legislative action against microplastics used in cosmetic products[87]. In this sense, experiments have been made using biodegradable polymers like polyhydroxyalkanoate (PHA), naturally occurring polymers like cellulose, inorganic compounds like silica or clay, natural compounds like corn starch, walnut powder, seaweed, tapioca etc. became particularly popular [84,85]

6.3.Other applications

Besides packaging and medical application, interest in biodegradable polymers grown in the agricultural sector. Some natural polymers, such as starch, cellulose, chitin, alginic acid, and lignin have been used in controlled release systems[11], ropes, and fishing nets[11] mulching to enhance sustainability[11]. Agricultural films placed in soil are susceptible to degradation and aging, and hence need to have some specific properties[11] to be a good alternative to solve agricultural pollution[1]. A well-known example of mulching films is starch, which when in contact with soil microorganisms, degrades into nontoxic products[11]. In terms of other applications, chitin acts as an absorbent for heavy and radioactive metals, which is useful in wastewater treatment[10]. Also, polyesters have been used in automotive, electronics, or construction sectors or disposable consumer products, e.g. cutlery and plates, and sanitary products[10].

7. Biodegradation implications on the environment

Finding the balance between durable and biodegradable materials is a great challenge. There is a need for long-lasting plastics (examples: aeronautical devices, construction materials, containers, etc., of great industrial interest) and short-lived biodegradable materials (examples: food packaging, medical devices, and agricultural covers). Therefore, the ideal would be to obtain materials that are resistant during their use but biodegradable at the end of their useful life. However, when biodegradable polymers are released into the environment in large quantities, different aspects must be considered.

Furthermore, water resources, not just drinking water resources, must be protected from contamination. The soil must also be preserved. Although the hypothesis is that composting is more environmentally friendly than material recovery, biodegradable materials have not been found to provide soil nutrition or soil structure benefits[88]. Biodegradable polymers do not have the proper nutrients for plants; they also degrade too quickly to act as a soil structure improvement component.

Another controversy involving the biodegradability of polymers is the production of hydrocarbon gases, mainly methane (CH_4) and ethylene (C_2H_4), which react with OH in the atmosphere and increase concentrations of carbon monoxide[89]. However, generating methane can be interesting if it is collected, as it can be used as biogas or to generate heat or electricity[90]. Therefore, the massive implementation of biogas collection systems in landfills can decrease the amount of methane emitted into the atmosphere. Additionally, methane gas shows a 23 times greater global warming potential than carbon dioxide, allowing methane collection and atmospheric diversion to mitigate the effects of climate change[91].

The introduction of new artificial biodegradable materials along with traditional biowaste can pose major risks to the production of compounds[30]. Due to the possibility of forming additional toxic compounds during biodegradation as a result of biotransformation, an assessment of toxicity is paramount when evaluating the biodegradability of polymers. Toxicity can be species-specific; we can find single-species tests, such as the earthworm acute toxicity test (OECD 207) and the terrestrial plant growth test (OECD 208), which are used for the toxicity of chemicals[41]. However, these tests are very limited, and tests performed for multi-species with model ecosystems provide information closer to the real fate of the compounds, but they are expensive and time-consuming to perform[92]. Ecotoxicity tests use model organisms under controlled laboratory conditions to ensure that no harmful degradation products are released into the environment[93]. The choice of test species depends on the ecosystem under investigation: for terrestrial environments, soil organisms, such as certain microbes[94], terrestrial plant species; for aquatic ecosystems, algae, crustaceans, and fish[95] are tested for their response to degradation products. Test systems differ in terms of duration and evaluated effects (lethal or sublethal, such as growth or reproduction, and specific responses, such as mutagenicity, carcinogenicity, neurotoxicity, or immunotoxicity)[92].

Since biodegradable polymers have been used in medical applications, there are many studies in the field of human toxicology. There are also some established standards for compostable plastics, which also include ecotoxicity requirements. For example, the European Standard EN 13432 requires data on growth and plant germination[96]. However, it should be mentioned that there is little ecotoxicological data on biodegradable polymers, and the assessment of the environmental impact of polymers is generally not covered by legislation such as that for chemicals.

Finally, it is worth mentioning that biodegradable polymers are equally dangerous to petrochemical derivative polymers, as it forms microplastics (100 nm - 5 mm size) or nanoplastic (NP) (<100 nm) that indirectly affect human health due to their deposition in various organs[36,97]. Additionally, biodegradable polymers are mainly disposed of in industrial composting, while conventional plastics are usually incinerated, recycled, or landfilled (banned in many western countries). Therefore, alternatives such as collection, sorting, and reprocessing capabilities are sustainable options that have less impact on the environment[98].

8. Conclusion and future perspectives

There are different challenges in the development of biodegradable materials, ranging from the complexity of their processing to the interest of consumers. Biodegradable materials have been associated with "bioplastics", which are bio-based plastics that are not necessarily degradable (e.g., green PE). Furthermore, the fact that biodegradability has been limited to industrial composting systems or negligible in the case of some bio-based plastics makes the process fragile. Therefore, we can confirm that it is extremely important that the ‘biodegradable’ label include a clear indication of the environment in which the test was carried out to have an adequate destination for its biodegradation to occur.

In addition, it is noted that the industry is constantly searching for cost-performance development of biodegradable materials to replace conventional plastics. However, there is still a great deficiency in infrastructure and the disposal of biodegradable materials.

In future perspectives, it is relevant to mention new approaches that have been explored, such as the addition of nano-sized materials (for example, starch, chitosan, protein, carbon nanotubes, and silver and clay nanoparticles) as a tool to improve the biodegradability rate of plastics. In addition, we can mention a line of development of new types of enzymes and microorganisms capable of rapidly metabolizing conventional plastics. However, it is important to emphasize that, in order to solve the problems of plastic waste, it is not enough to "hide" them, micro and nano-sized plastics, despite not causing visible pollution, can be extremely harmful, resulting in serious effects on the environment, human health, plants, and animals. Therefore, future research should focus on discovering strategies to remediate these small particles in the environment and in living things.

Finally, it is worth noting that although there are many challenges still to be overcome, there is a race from different sectors in search of differentiated solutions for the accumulation of plastic waste.

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8 Authors Contribution

La Fuente C.I.A.: Conceptualization, investigation, data collection, writing - original draft, Funding acquisition.

Maniglia B.C.: Conceptualization, investigation, data collection, writing original draft. Funding acquisition.

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Figure captions

Figure 1. Scheme representing the stages of biodegradation.

Figure 2. Tests for biodegradability determination of solid polymers.

Figure 3. Papers involving biodegradable polymers and their applications in the last 5 years **(A);** and their progress over the years **(B)**; Schematic representation of the main biodegradable polymers and their applications. Adapted from[66] **(C)**. **Note.** The literature search was performed on the Web of Science® database on 14 February 2022.

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