

Review

Biodegradation of Hemicellulose-Cellulose-Starch-Based Bioplastics and Microbial Polyesters

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Abstract: The volume of discarded solid wastes, especially plastic, which accumulates in large quantities in different environments, has substantially increased. Population growth and the consumption pattern of societies associated with unsustainable production routes have caused the pollution level to increase. Therefore, the development of materials that help mitigate the impacts of plastics is fundamental. However, bioplastics can result in a misunderstanding about their properties and environmental impacts, as well as incorrect management of their final disposition, from misidentifications and classifications. This chapter addresses the aspects and factors surrounding the biodegradation of bioplastics from natural (plant biomass (starch, lignin, cellulose, hemicellulose, and starch) and bacterial polyester polymers. Therefore, the biodegradation of bioplastics is a factor that must be studied, because due to the increase in the production of different bioplastics, they may present differences in the decomposition rates.

Keywords: biodegradation; bioplastics; lignocellulosic fibers; microbial polyesters



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1. Introduction

Consumption demands for industrialized materials such as plastics in their various applications have increased over the past years. This consumption is generating residues, which require alternatives for their proper disposal and recycling. Disposal, recycling, and plastic substitution are potential research areas towards urgent and necessary solutions. Most commercial plastics come from the petrochemical industry, which uses natural gas and fossil hydrocarbons as feedstock. Such synthetic plastics are biodegradable and degradable only for a long period. Therefore, they are considered neither biodegradable nor renewable [1]. Synthetic polymers, such as polypropylene (PP), polyethylene (PE), polytetrafluoroethylene (PTFE), nylon, polyester (PS), and epoxy are examples of plastic components of high resistivity, chemical and biological inertness, resistance, flexibility, and other interesting properties [2–5].

At the beginning of the large-scale production of synthetic plastic materials, their properties seemed adequate for good quality development. However, such materials are non-biodegradable, thus generating large accumulations of residues in different landscapes. Thus, they have been a cause of growing concerns due to environmental problems. New materials based on biological sources have been developed towards solving or reducing the above-mentioned problems. However, in addition to be renewable and biodegradable, bioplastics must have vapors barrier properties and mechanical properties that meet the different applications of this material, and the attention has now evolved towards the possible ecotoxic effects of bioplastics and active properties for a cover of food.

The names of biodegradable and/or bioplastic products given by companies and reported in the literature, when drawn up wrongly, can lead to misunderstandings by the general public due to incorrect classifications of the polymeric materials [6–9]. A bioplastic

can be biodegradable or not. However, a biodegradable material does not necessarily come from a biological source. Towards the avoidance of errors, the following definitions, reported in this article, must be clarified:

- Plastics are polymeric matrices comprised of organic polymers of high molecular weight and other substances, such as fillers, colors, and additives [6]. In general, the synthetic route is predominant in the synthesis of the material.
- Bioplastic refers to materials that are biodegradable, bio-based, or both. Although the term bioplastic is generally used to distinguish polymers derived from fossil resources, it is worth mentioning that bioplastics may come from petroleum [6]. The prefix “bio” of bioplastic does not necessarily mean this material is environmentally friendly [6].
- Biomass is a source of natural organic carbon that may originate from animals or vegetables raised/cultivated by humans or that spontaneously emerge in terrestrial and marine environments [10].

Different biotic and abiotic factors contribute to the different degradation processes [11]. Thermal, mechanical, and chemical degradation, as well as photodegradation, are examples of abiotic degradation. A degradation process is related to the fragmentation of material into small elements or molecules, or just physical and chemical changes in a polymer. Due to high temperatures, polymers can be thermally degraded. The chemical bonds in their chains are broken by a thermo-degradation effect [12].

Mechanical degradation is an abiotic degradation mechanism that occurs through shear forces (due to aging, turbulence in water and air, snow pressure, and other factors), tension and/or compression. Under environmental conditions, it acts synergistically with different abiotic factors [13].

Abiotic chemical degradation occurs by the degradative effect of chemicals substances, and represent one of the most important mechanisms of abiotic degradation, since the polymer matrix is affected by atmospheric or agrochemical pollutants, such as oxygen (i.e., O₂ or O₃), which produce free radicals through oxidation, attacking covalent bonds [13]. Abiotic chemical degradation differs from biotic chemical degradation, mainly regarding the origin of the chemical with a degrading effect.

Photodegradation is the process of degradation of polymers by the action of light, resulting in the oxidation of the material. UV rays interact with chromophores groups of polymers (carbonyl, hydroxyls, and aldehydes), which are degraded by chain fission, photoionization, crosslinking, and oxidation reaction [11,13–15].

Microbial biodegradation is a degradation process of polymers and other materials through the action of microorganisms [11] resulting in CO₂ and/or methane, water, cell biomass, and energy. However, in the natural environment and even in the process of controlled biodegradation, abiotic effects help or even occur synergistically with biodegradation. This consideration of synergism is important for the elaboration of biodegradation procedures.

With environmental concern, this review evaluated the biodegradation process (considering the synergistic action of biotic and abiotic agents) of bioplastics elaborated with polysaccharides from plant biomass and microbial polyesters. Moreover, addressing the definitions, biodegradation mechanism, and factors that affect the biodegradative process of bioplastics. The scope of this review does not address the biodegradation of bioplastics produced from polymers of animal origin (natural polymer), and bioplastics derived from petroleum (PBAT, PBS, PVA, PCL, and PGA [16]. However, the definitions presented in this review do not exclude these types of bioplastics.

2. Problems Related to Plastics

The current geological era, the so-called Anthropocene, is exposed to the influence of human actions in different environments. Indicators from such anthropic actions are biodiversity reduction, deforestation, climate, and other environmental changes [17]. However, materials produced by human society, like plastics, are also indicators of the Anthropocene.

Plastics directly (i.e., environmental impacts from the plastic production chain) affect different environments (e.g., terrestrial and marine).

An environment in which plastic waste currently generates several problems, is the oceans, due to the large accumulation of these materials. The plastic that reaches the oceans mostly is generated in coastal population regions, where the disposal and management of this waste is destined for uncontrolled landfills [18]. Due to urban runoff and inland waterways, such plastics reach oceans and are transported via tide and winds. It is estimated that between 4.8 and 12.7 million metric tons of plastics produced in the continent (distribution varies according to the analyzed location) reached the marine environment in 2010 [18].

In recent years, environmental concerns (e.g., harmful effects of plastics on the environment, since they are not biodegradable [19], or slowly degraded) have been intensified. Large accumulations of floating plastics in the oceans have been reported- approximately 1.8 trillion pieces of plastic have been quantified in the Great Pacific Garbage Patch (GPGP) [20]. The ingestion of plastic fragments by the marine fauna is a major concern due to their small size [18,21,22], the so-called microplastics, which are smaller than 5 mm [21]. Besides, since plastic fragments are present on the surface and floor of oceans, as well as in several maritime regions (coastal areas) and the Arctic sea ice, strategies, as a reduction in inputs [18] and the elaboration/utilization of biodegradable materials, would be adequate measures to reduce the impacts of plastics.

Even with the area of studies on the impacts of plastics on fauna and for the various organisms still under development, some studies point to the occurrence of toxicological effects of this synthetic waste [23,24]. A plastic intake and entanglement can lead to the lower life quality of organisms, loss of mobility, external and internal injuries, blockage of digestion, and other harms [25]. Goldstein and Goodwin [22] identified the presence of microplastics (mainly PE, PS, and PP) in the digestive tract of 33.5% of *Gooseneck crustaceans* (*Lepas* spp.).

The development of innovative technologies represents a means for both sustainable development and the growth of emerging countries, such as Brazil, whose sustainable energy has been highlighted by innovation technologies. Thus, even with bioplastic not representing a material for total replacement of non-biodegradable plastic, researches and production of bioplastics are a technological alternative for the development of a more sustainable and balanced society. Therefore, aligning with the current trend (socio-political and environmental), in which concerns with the environment is growing.

3. Biodegradation Process

The microbial biodegradation of materials occurs by the action of microorganisms, such as fungi and bacteria [26], and is classified as physical, chemical, and enzymatic according to modifications in the materials. Biodegradation is a natural process of vital importance for nutrients and energy recycling [27]. Microorganisms use organic material as a source of nutrition for their metabolism; except for the substances used in metabolic incorporation, the rest is oxidized by cellular respiration, thus leading to the formation of simple and small submetabolites, released in the environment [28,29].

Biodegradation due to physical degradation occurs from the adhesion of microorganism species to the surface of organic materials through the secretion of a gum [30] produced by microorganisms. This gum represents a complex matrix made of natural polymers (e.g., polysaccharides and proteins). Such a thick complex, together with microorganisms, infiltrates the material and changes its volume, size, pores distribution, moisture content, and thermal transfers. A few microorganisms (e.g., filamentous fungi) lead to cracks in the materials due to mycelial growth, i.e., both their durability and resistance properties are reduced [13,31]. Microorganism biofilms are a matrix that protects microorganisms from different environmental conditions and results in a major change in materials [13,32].

Biodegradation by chemical degradation refers to the production of chemical substances by living organisms, which facilitate and increase the speed of the process. Emulsi-

ifying substances produced by microorganisms help the exchange between hydrophobic and hydrophilic phases, which are important interactions for the penetration of microorganisms in the polymeric material [33]. Such a lime formation (polymers secreted by microorganisms mixed with different microbial species) improves the material deterioration. It represents a point of accumulation of polluting and chemical substances (abiotic chemical degradation), thus benefitting microbial proliferation [34].

Examples of chemical substances released into the environment by microorganisms, which play an important role in chemical biodegradation, are nitrous acid, nitric acid, and sulfuric acid. All of these compounds are produced by chemolithotrophic bacteria, such as *Nitrosomonas* spp., *Nitrobacter* spp., and *Thiobacillus* spp., respectively [29,33,35]. Apart from the action of chemical substances generated by those organisms, chemoorganotrophic microorganisms generate organic acids with potential for chemical degradation (e.g., oxalic, citric, gluconic, glutaric, glyoxalic, oxaloacetic, and fumaric acids).

The action mechanisms of such acids (organic or inorganic) are diverse and include an increase in surface erosion when adhering to the material surface [36]. The use of those acids as nutrients benefits the growth of filamentous fungi and bacteria [13]. Another action mechanism of biotic chemical degradation is the oxidation of organic material. Certain fungi and bacteria have specific proteins in their membrane that capture iron-chelating compounds (siderophores) [37]. With this mechanism microorganisms capture cations from a matrix.

Biodegradation by enzymatic degradation occurs due to the depolymerization of polymeric chains of a matrix through the action of hydrolase enzymes that catalyze the reactions of chemical bonds breakage adding a water molecule. These bonds are ether, peptide-like, and ester, present in biodegradable bioplastics. The main enzymes are amylases and cellulases, which cleave starch and cellulose polymers, respectively. However, other enzymes (breakage of ester bonds), such as esterases and lipases, can degrade co-polyesters.

A mechanism that explains the action of hydrolases (e.g., depolymerase) in polyesters hydrolysis (synthetic and natural) through biodegradation is related to three amino acids, namely serine, histidine, and aspartate. A hydrogen bond is formed when a component reacts with the histidine ring, thus guiding interaction between histidine and serine, and forming an alcohol group of high nucleophilic character (-O). Histidine plays a deprotonating role for serine, i.e., as a base. The alkoxide group includes an ester bond and generates an acyl-enzyme and an alcohol group. Finally, a free enzyme and a terminal carboxyl group are generated by the action of the water molecule under an acyl-enzyme. This entire enzymatic degradation process is termed catalytic triad [30,38,39], and the products generated are metabolized or not by microorganisms that have depolymerizing enzymes. Therefore, a consortium of microorganisms is important for complete biodegradation [13]. Figure 1 depicts the mechanism of action of depolymerizes and the catalytic triad.

Apart from the biodegradation of cellulose, starch, and polyesters, hemicellulose is another polymer that can be degraded by microbial enzymes. A catalytic action of hemicellulases (enzymatic pool) on different types of hemicellulose polysaccharides produces monomeric sugars, acetic acids [40]. For example, enzymes that degrade xylan (hemicellulose from grasses) are endo-1,4- β -xylanase (cleavage results in oligosaccharides), xylan 1,4- β -xylosidase (cleavage of oligosaccharides generate by xylan, which forms xylose monomers), and accessory enzymes, such as xylan-esterases, ferulic and p-coumaric-esterases, α -L-arabinofuranosidases, and α -4-O-methyl glucuronidase [41]. Both enzymes act synergistically so that xylans and hemicellulose mannans of some types of plant cell walls are depolymerized [42]. Nevertheless, some polymers are not biodegraded by common enzymatic hydrolysis, i.e., polymers can be oxidized by enzymes such as laccase, dioxygenase, peroxidases, monooxygenase, and oxidases [43]. Thus, such enzymes are not hydrolases and influence the cleavage process of polymers differently from hydrolases (oxygen insertion, hydroxylation, oxidation, and free radical formation lead to polymer cleavage) [43]. Figure 2 depicts the enzymatic biodegradation process.

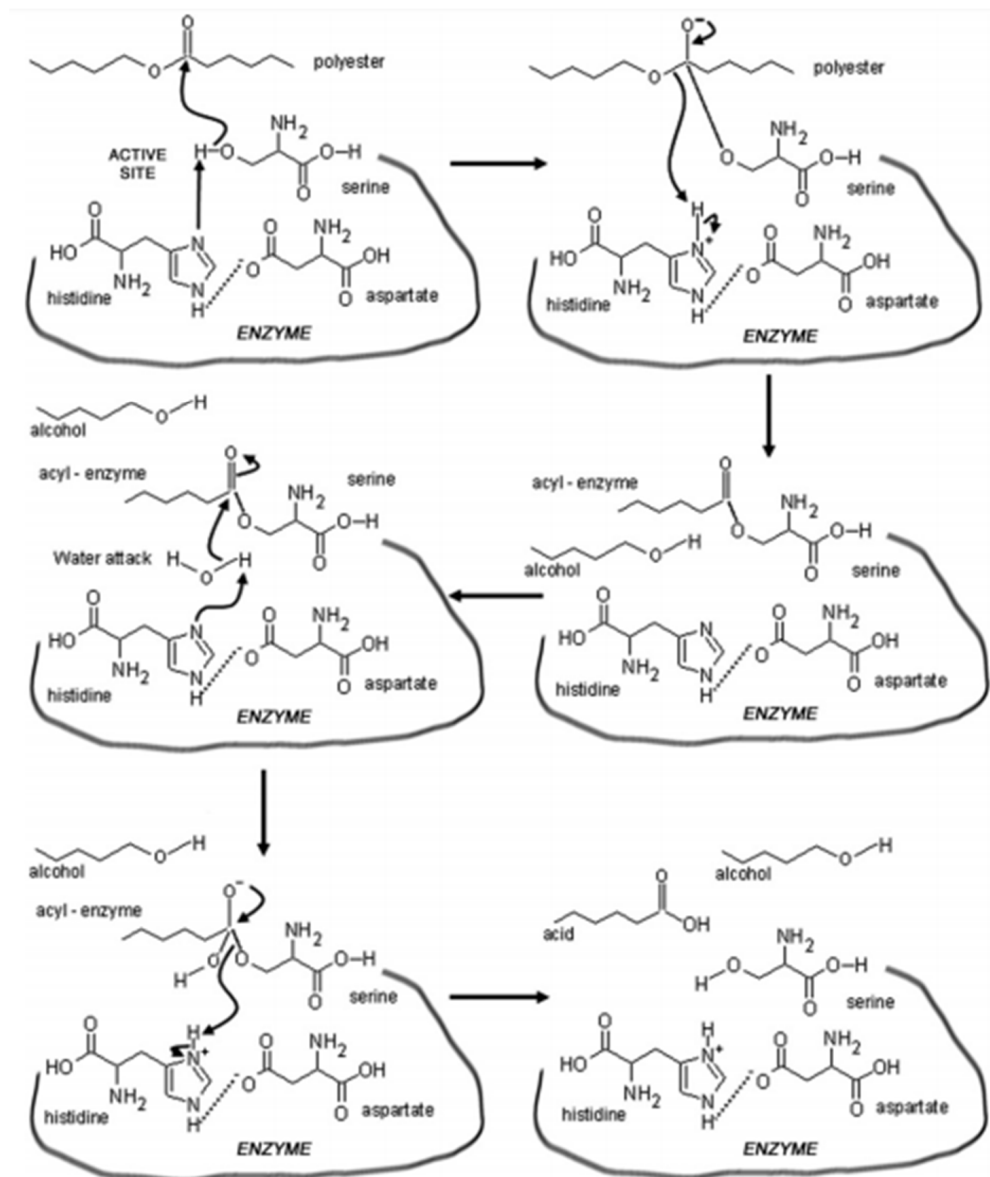


Figure 1. Enzymatic hydrolysis of polymers and catalytic site of depolymerase enzymes [13].

The result of biodegradation, for example of bioplastic from natural polymers (e.g., polysaccharides) is the generation of small molecules from a polymer. Microorganisms cannot employ large substances insoluble in water for obtaining organic or inorganic nutrients for their metabolism. They produce enzymes and chemicals used in extracellular environments and, therefore, depolymerize the materials. After hydrolysis and/or oxidative action of microorganism enzymes on different polymers, which results in monomers, metabolism oxidation occurs. In this system, organic compounds lead to a loss of electrons and the consequent production of ATP molecule (adenosine triphosphate). This is the last biodegradation stage, in which organic matter is mineralized. The microorganisms use smaller and simple organic molecules, such as oligomers and monomers, for their metabolic activities. However, byproducts are generated from microbial metabolism (e.g., carbon dioxide— aerobic degradation), water, biomass, methane, and hydrogen sulfide (anaerobic degradation) [45,46]. Figure 3 displays the biotic and abiotic degradation of plastic.

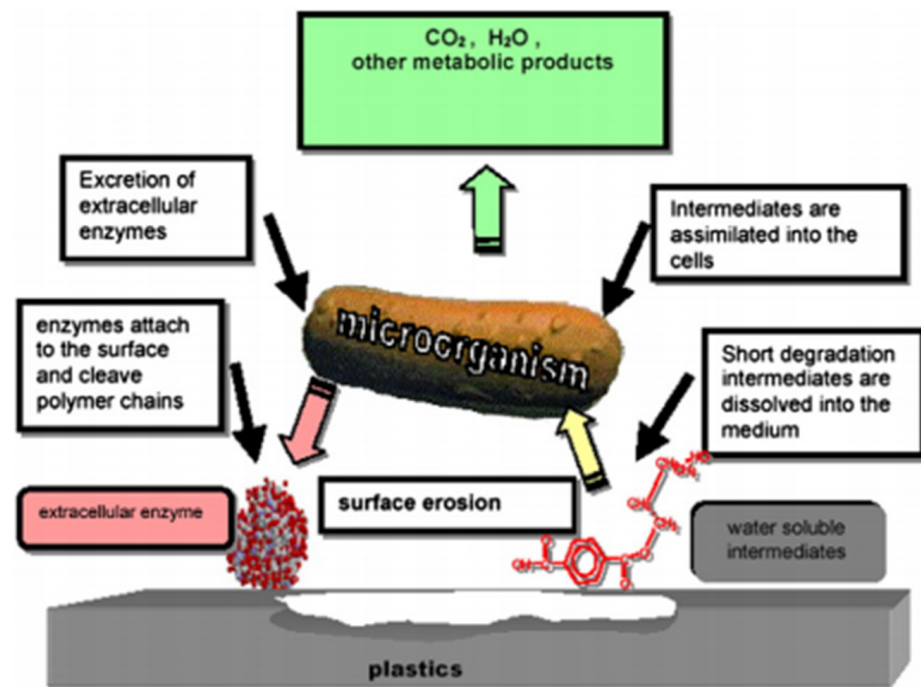


Figure 2. Enzymatic biodegradation process [44].

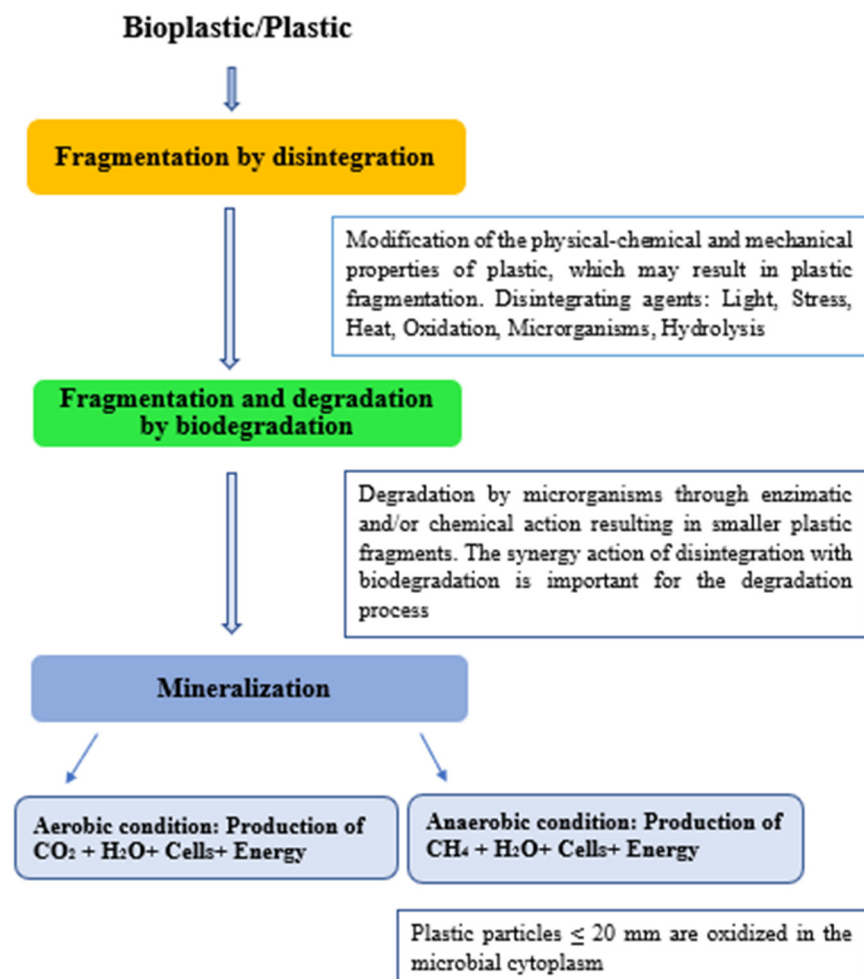


Figure 3. Disintegration, biodegradation, and mineralization process of plastic polymeric materials. Adapted [47].

3.1. Factors That Influence Biodegradation

The microbial population available is a key factor for biodegradation in an environment (soil, air, and water), and several properties (e.g., the chemical constitution of materials) affects the efficiency of the biodegradation process. Chemical composition influences the biodegradation of plastics through different patterns of crystallinity, hydrophilic and hydrophobic character, conformational flexibility, polymer accessibility, surface area, molecular weight, melting temperature, hydrolyzable and oxidizable bonds in polymer chains, morphology, and stereoconfiguration [27,48,49].

Crystallinity influences biodegradability because it affects the accessibility of the enzyme to the material polymer. More organized regions of polymers (crystalline) tend to hinder enzymatic hydrolysis since catalytic proteins diffuse with greater difficulty. On the other hand, water molecules diffuse more easily between amorphous (less organized) regions, and enzymes can easily access the material polymers in such regions [28].

The polarity of bioplastics directly influences biodegradation, since materials developed with hydrophobic polymers are less susceptible to enzymatic attack. Degrading microorganisms depend on a hydrophilic surface to adhere to and catalyze the depolymerization reaction by means of hydrolytic enzymes. However, this enzymatic accessibility to the material is reduced on hydrophobic polymeric surfaces. This impediment occurs not only because the microorganisms and enzymes are more hydrophilic, but also due to the aqueous medium (usual water), in which the enzyme is contained, to have their contact with the material (bioplastic) reduced. For example, glycolic polyacids (PGA) are more easily biodegraded than poly (lactic acids) (PLA), since PLA is more hydrophobic [50].

Blends in a polymeric bioplastic matrix are common when it is desired to obtain materials with certain characteristics, and also interfere with biodegradation (increase or reduce biodegradation), since the different components of biocomposites can influence the accessibility of the enzyme to the polymeric material in different ways.

The molecular weight of polymers affects the biodegradability of plastics, since the heavier the molecular weight, the greater the difficulty for microorganisms to break it down and assimilate. Therefore, the lower the molecular weight of the polymer, the easier the biodegradation, since the need for extracorporeal digestion is reduced. Aliphatic polyester is one of the few biodegradable polymers of high molecular weight [13]. However, it is worth mentioning that in addition to the molecular weight, the types of bonds in the polymeric chain (considering that bioplastic, like plastic, is formed by a polymeric matrix), and different chemical groups in polymers influence the biodegradation process.

Although the term “bio” degradation is directly correlated with the fragmentation of a polymer by the action of microorganisms, these microorganisms do not act in isolation on the polymeric material, since abiotic agents influence the fragmentation efficiency. The abiotic degradation of organic matter such as thermal, mechanical, chemical, and by the action of light are examples of degradative processes. These processes work synergistically with biodegradation, reducing the material to dimensions that allow microbial assimilation [13,51].

3.2. Assessment and Biodegradation Quantification

Biodegradation can be measured through metabolic products, physical and chemical properties of plastics/bioplastic, acidification of the medium, and other ways. CO₂ is a product of biodegradation, more specifically, of the oxidation of organic matter, and can be used for direct or indirect measurement of material biodegradation over a period of time. Its content released in a degradation process is quantified by the respirometry technique, which can use a closed CO₂ production and a capture system. International methods, such as ASTM D5338-15 [52] and ISO 14855-2: 2018 [53] are applied for the quantification of the CO₂ produced in a microbial degradation process.

The measurement of consumed oxygen (ISO 17556: 2003) [54] is another method of quantifying biodegradation by respirometry. Respirometry involves techniques that measure parameters indicative of cellular respiration. The higher the consumption of

oxygen and the release of CO₂ by microorganisms, the better the biodegradation indicator. For details and examples of other standard methods of respirometry analysis (ASTM, EN, and ISO), see specialized literature [55].

Methane molecules can also be used for measurements of materials biodegradation. However, unlike the above-mentioned respirometry techniques, CH₄, CO₂, and other gases quantification is generally conducted under anaerobic conditions. Analysis methods such as ASTM D5511-02 [56], is used for this purpose.

Apart from microbial proliferation in plastic/bioplastics materials, analyses of color change, surface roughness, cracks, and holes are also alternatives for checking the deterioration of materials [13,36]. Analysis parameters can be used especially for materials of difficult biodegradation and low CO₂ release. However, the results of such analyses (e.g., microbial growth in the polymeric matrix) are not recommended for the conclusion of biodegradation or abiotic degradation directly [13]. Additional techniques, such as electron microscopy, photon microscopy, microscopy of polarization, and atomic force microscopy reinforce the results [13,57,58].

The physical properties of plastics/bioplastics (e.g., tensile strength, elongation at break, modulus of elasticity, crystallinity, cold crystallization temperature, and glass transition temperature) can be measured as biodegradation indicators. The weight loss of a sample determined by the burial method can be used in plastic/bioplastic biodegradation analyses, although it may result from the solubility and volatility of certain substances [13]. The analysis of weight loss of bioplastics by burying in soil, or composting systems, may result in conclusion errors, since in addition to the mass of the soil or compost account for the variation in the bioplastic mass, in bioplastics washing processes (a step which precedes weighing procedures), can cause fragmentation and loss of material derived from bioplastic. Thus, even though the method of analyzing mass loss is frequently reported in the literature, as is usual in determining the biodegradation of bioplastics, this technique ends up being difficult to perform [59]. Recent articles evaluating the biodegradation of bioplastics by burying in soil and compost has used image evaluation as a tool for analysis, that is, the reduction of the area of bioplastics, detected by image registration (from the insertion of the bioplastic in a mold/grid with known dimensions) [60,61].

The indication of biodegradation through products generated by microorganisms is another way of measuring the process. For example, the biodegradation of polymeric cellulose materials can be measured according to the release of glucose [62], or the quantification of 1,4-butanediol as an indicator of the biodegradation of PBA and PBS polymers [63].

The increase in microbial biomass (weight or number of cells) is indicative of a biodegradation process since a single source of carbon (plastic or bioplastic material) in a closed environment can point out the occurrence of biodegradation and/or surface changes and molecular rearrangements. However, conclusive statements about the amount of mineralized material cannot be directly made.

The evaluation and quantification of bioplastic and/or plastic biodegradation by the above-mentioned methods can be conducted in an aqueous medium and soil. However, each condition of analysis imposes different requirements, which leads to different responses from different methods.

3.3. Biodegradation of Bio-Based Polymers Bioplastics

In this topic, biodegradation of bioplastics developed with polysaccharides from plant biomass/lignocellulose and microbial polyesters was followed as the scope of this review. It was exemplified the biodegradation of a category of bioplastics, those developed with natural polymers (vegetable and microbial). Therefore, this review does not intend to address issues related to the development of bioplastics of vegetable and microbial origin, advantages and disadvantages in addition to the viability of this material (related to the economic aspects and properties of bioplastics). To obtain this information, it is recommended reading of the specialized literature [6,64–66].

3.3.1. Biodegradation of Plant-Based Polymers Bioplastics

The mass loss of bioplastics from rice straw showed complete degradation after 105 days [67]. Rice straw bioplastics were composed mainly of cellulose and trifluoroacetic acid. On the first day of contact with the soil, the bioplastic showed an increase in mass, due to the phenomenon of water absorption by the material. According to the authors, its mechanical properties are similar to those of polystyrene (bioplastic in the dry state).

The mass loss of bioplastics consisting of acetylated starch and acetylated sugarcane fibers (lignin, hemicellulose, and cellulose) resulted in 24.2 to 39.3% degradation after 5 weeks [68]. The acetyl group may have created stable biodegradable sites; however, an increasing effect on the crystallinity of the bioplastic with the addition of cellulose may have contributed to the low biodegradation rate due to the restriction effect of the microbial enzyme's activity. In addition to the crystallinity and chemical structure of cellulose, microbial diversity, carbon availability and the period of biodegradation considered can influence its depolymerization.

Bioplastics (glycerol, acetylated starch, and acetylated nanocellulose composition) subjected to biodegradation in a petri dish with *Trametes versicolor* were completely degraded in 60 days, and after 40 days with starch and non-acetylated reinforcement. The starch bioplastics were completely biodegraded after 30 days, and the addition of cellulose to the formulation of bio-based plastics resulted in a longer biodegradation time [69]. Water and moisture absorption is important in the biodegradation process of bioplastics [70]. The starch-based bioplastics investigated in this study were composed of different concentrations of oxidation starch (20, 40, and 60%). Oxidation decreases biodegradation due to reduced swelling and water absorption from the soil by bioplastic.

Hemicellulose is another natural plant-derived polymer of potential application for the development of bioplastics. However, in addition to the elaboration that biomaterial, the study of the biodegradation of these carbohydrates in bioplastics have not received attention, as the area of use of hemicellulose for bioplastic focus on physicochemical properties and modifications of this macromolecule. The bioplastic based on xylan (of the hemicellulose type of grasses) and blended with gelatine was completely biodegraded after 15 days of conditioning (determined by the burial procedure) [71]. This bioplastic was considered 100% biodegradable since the sample could not be recovered for weighing. A bioplastic made with 50% xylan (from beechwood) and PVA (polyvinyl alcohol) was 56% biodegraded after 30 days by burial in soil [72]. PVA reduced the biodegradation of the bioplastic produced by the PVA/xylan mixture. The sample with 25% xylan was 42.2% biodegraded after 30 days of burial in soil.

Xylan was grafted with poly-(ϵ -caprolactone) (PCL), and biodegradation was evaluated by BOD (biological oxygen demand). The biodegradation (aerobic and activated sludge) kinetics of bioplastics with high concentrations of PCL was delayed in comparison to materials made with pure hemicellulose or with lower graft concentrations [66]. Despite changes in the kinetics, the biodegradation property of the bioplastic was not altered and ranged between 95.3 and 99.7%.

Recalcitrant substances also influence the biodegradation of natural polymers. Lignin is a constituent of lignocellulosic fibers, shows the highest degree of recalcitrance in the plant cell wall [73,74]. This polymeric complex of phenylpropane units hinders the biodegradation of the material or products that contain it, such as bioplastics, and reduces the contact surface of lignocellulosic fibers with degrading enzymes [74]. Lignin requires different enzymes to degrade due to the different units that comprise its polymeric complex [75]. In anaerobic environments lignin may persist biodegradation for a longer time, with this process is primarily more efficient in aerobic environments [76], due to the catalytic action involved in oxygen.

Starch and lignin (lignosulfonate) bioplastics were completely biodegraded after 4-month burial [77]. Biodegradation was measured through the analysis of CO₂ and morphological characteristics. The samples with lignin analyzed after 5 weeks of biodegradation tests were fragmented, however, small residues of the bioplastic were identified.

After the 2-month burial, the samples with lignin showed a significant biodegradation effect, with small fragments of the material still observed. After 4 months of testing, residues of bioplastic fragments were no longer detected. A bioplastic made from the addition of lignin (1.2% *w/t*) to the bio-PTT matrix (Bio-poly (trimethylene terephthalate)) increased its weight loss through biodegradation in soil [78]. In 140-day burial, bio-PTT/lignin bioplastic showed more than 50% mass weight loss.

A higher CO₂ emission was reported from films with lignin in comparison to the bioplastic composed only of starch, due to the greater amount of carbon atoms in its formulation [77]. However, such CO₂ may have originated from the metabolism of soil organic compounds, i.e., the bioplastic may have stimulated the microbial degradation of stable organic compounds in the soil through the priming effect. A strategy for the biodegradation of bioplastics composed of lignin, due to the recalcitrance of this phenolic complex, is the application of UV radiation prior to chemical, microbiological and/or enzymatic treatments. Lignin is susceptible to photodegradation due to the UV effect [79]. After photodegradation, other treatment combinations can be applied for the degradation or biodegradation of lignocellulosic fibers, such as enzymatic or oxidative treatments. One of the advantages of using lignin in the development of thermoplastic formulations is its processing at high temperatures [80]. However, studies using lignin in the bioplastic formulation, have not received much attention.

3.3.2. Biodegradation/Enzymatic Degradation of Plant-Based Polymers Bioplastics in Relation to Derivatization

The assessment of biodegradation, disintegration, and enzymatic degradation of bioplastics made with natural polymers (such as proteins, starch, cellulose, and hemicellulose) is not recurrent in the literature. Biodegradation has received lower attention when compared to the objective of most studies, which is to evaluate the physicochemical and mechanical properties of the materials. However, this limitation in the studies is even greater when compared to the biodegradation of bioplastics made with modified polymers.

The comparison between bioplastics developed from unmodified and modified hemicellulose presents few studies intending to analyze the enzymatic degradation [81], and biodegradation. This low number of studies with hemicellulose could be related to the difficulties in obtaining a plastic polymer matrix from this heterogeneous vegetable polysaccharide. However, in addition to the analysis of the physicochemical properties of modified bioplastics, the effects of chemical, physical, and biological (and enzymatic) modifications of polymers on biodegradation must be considered. The enzymes involved in the enzymatic degradation of unmodified and modified polysaccharides may be different. Moreover, a more complex enzymatic pool will be required for modified polysaccharides.

As pending groups are attached to the polysaccharides chain, new enzymes will be required for further hydrolysis. According to a recent review article, physical modifications of polysaccharides hardly result in a change in the biodegradation process [82]. However, chemical changes result in different degradation mechanisms. Considering a chemical similarity, the enzymatic degradation of cellulose acetate can be catalyzed by acetyl esterases, an enzyme common for xylan deacetylation. The modification or functionalization of polysaccharides may result in a reduction in biodegradation since modified bioplastics (acetylated cellulose, acetylated xylan, acetylated starch, starch propionate, starch butyrate, starch valerate, and starch hexanoate) showed a reduction in anaerobic biodegradation [83]. For example, the degree substitution (DS) > 1.5, 1.5, 1.2 for starch, cellulose, and modified xylan (acetylated) respectively, represented the minimum modification necessary to delay the biodegradation of bioplastics.

The chemical modifications of the polysaccharides that make up bioplastics, such as acetylation, increase the degree of hydrophobicity of the polymers and the plastic matrix. This has the advantage of reducing the solubilization of the polymers in polar solutions. However, resulted in a decrease the enzymatic degradation. It was observed a reduction in two mannases of *Cellvibrio japonicus* (CjMan5A and CjMan26A), with reduced catalytic activities on galactoglucomannan substrates (hemicellulose) due to the decrease

of the solubility of the polymers [81]. Other studies in the literature showed the influence of chemical modification of hemicellulose in relation to solubility, thermal resistance, crystallinity [84], and biodegradation rate [85]. Therefore, the diffusion of water by the composite and biodegradation is a parameter affected by chemical derivatization.

Modified xylans with an increase in the DS reduced enzymatic degradation by xylanolytic enzyme [86]. However, a rapid biodegradation rate (80%) on the first day of the evaluation was achieved for (hydroxypropyl)xylan. Substitutions above 1.5 reduced enzymatic degradability by 10%. However, the modification of cellulose with hydroxypropyl led to a reduction in biodegradation (20% in 18 days). Regarding the DS and the enzymatic activity, the article justifies the limitation of the recognition of the xylanolytic enzyme to the substrate due to chemical modification. In addition to the sterile impediment, when it changes the polysaccharide polarity through modification, it may be another explanation for the degradability reduction [87].

Modifications of polysaccharides may result in a less hydrophobic bioplastic, favoring the process of biological and abiotic degradation. Xylan carboxymethylation for bioplastic production showed an increase in water absorption at high relative humidity, demonstrating, therefore, the hydrophilic character of the carboxymethyl groups [88]. Carboxymethylation is a procedure for the production of hemicellulose-based bioplastics with increases in hydrophilic characteristics [89]. This procedure results in the development of environmentally favorable materials considering biodegradation.

A modification of hemicellulose by subtraction of chemical constituents may result in a different biodegradation process. An enzymatic modification of arabinoxylan resulted in an increase in the bioplastic crystallinity as the arabinose content was reduced [90,91]. In both of these studies, the effects of enzymatic modification of hemicellulose in relation to biodegradation were not evaluated. However, the increase in crystallinity may be a retarding factor in the bioplastic biodegradation due to the degree of organization of the molecules limiting enzymatic action, probably reducing the water absorption effect and reducing microbial growth.

The different modifications in natural bio-based polymers (for example, polysaccharides) may result in a difficulty in biodegradation or enzymatic degradation. The rate of degradation of these materials can reduce in a given period. However, the material can still be metabolized or degraded using enzymes. For example, acetylated xylan is the form found in natural lignocellulosic materials, therefore, although acetyl groups result in a delay in biodegradation, these polysaccharides are biodegradable by microbial enzymes, such as xylanases and esterases, whereas the acetylated xylan form is predominant in the environment.

3.3.3. Biodegradation of Microbe-Based Polymers Bioplastics

Under the nutritional abundance of carbon and nitrogen, some bacteria can synthesize energy reserve polymer (inclusions). Polymers like polyhydroxyalkanoate (PHA) (intracellular granules), can be produced via microbial fermentation of biomass (animal or vegetable). Regarding applications, these natural polymers are an important alternative for the manufacture of bioplastic materials since they are biodegradable and biocompatible, and used in the medical field [92]. With the 41% increase in world production of PHAs between 2010–2017, this polyester has become a polymer of significant interest in the development of bioplastics. The properties of this microbial polyester can contribute to a reduction of environmental impacts due to the closed carbon cycle generated by biodegradation [93].

There is a growing interest in the development of materials formulated with PHAs, the study of the biodegradability of these materials. However, factors that influence the degradation of composites and bioplastics are necessary. Some of the marine microorganisms that are known to degrade PHAs [94] are *Aestuariibacter halophilus* S23; *Alcanivorax* sp. 24; *Alcanivorax dieselolei* B-5; *Pseudoalteromonas haloplanktis*; *Alteromonas* sp. MH53; *Bacillus* sp.; *Bacillus* sp. strain NRRL B-14911; *Bacillus* sp. MH10; *Comamonas testosteroni* YM1004;

Enterobacter sp.; *Aliiglaciecola lipolytica*; *Gracilibacillus* sp.; *Marinobacter* sp. NK-1; *Nocardiopsis aegyptia*; *Pseudoalteromonas* sp. NRRL B-30083; *Pseudoalteromonas gelatinilytica* NH153; *Pseudoalteromonas shioiyasakiensis* S35; *Pseudomonas stutzeri* YM1006; *Psychrobacillus* sp. PL87; *Rheinheimera* sp. PL100; *Shewanella* sp. JKCM-AJ-6,1 α ; *Streptomyces* sp. SNG9. Terrestrial microbial representatives degraders PHAs [95] are *Alcaligenes faecalis*; *Pseudomonas lemoignei*; *Acientobacter* sp.; *Acientobacter schindleri*; *Bacillus* sp.; *Pseudomonas* sp.; *Stenotrophomonas maltophilia*; *Variovorax paradoxus*; *Stenotrophomonas rhizophilia*; *Penicillium* sp.; *Purpureocillium lilacinum*; *Verticillium lateritium*; *Burkholderia* sp.; *Nocardiopsis* sp.; *Streptomyces* sp.; *Bacillus cereus*; *Burkholderia* sp.; *Cupriavidus* sp.; *Gongronella butleri*; *Penicillium oxalicum*.

As in polysaccharide-based bioplastics, crystallinity in polyester bioplastics from microbial synthesis plays an important role in the biodegradation process. In bioplastics with higher proportions of amorphous regions, depolymerization occurs more quickly through abiotic or biotic action. For example, higher biodegradation was obtained with hydroxybutyrate (PHB), hydroxybutyrate-co-hydroxyvalerate (PHBV-40), PHBV-20, and P (3HB, 4HB) (10% mol of 4HB) and PHBV-3 [96]. According to the quantification of CO₂ in a composting vessel, PHBV-40 and P (3HB, 4HB) (10% mol 4HB) showed the highest degrees of biodegradation, due to a reduction in crystallinity with the addition of higher percentages of HV (valerate hydroxide—indicated by the numbering in front of the acronym) and 4HB. Biodegradation was 90.5%, 89.3%, 80.2%, 90.3% and 79.7% in 110 days of analysis for bioplastics formulated by PHBV-40, PHBV-20, PHBV-3, P (3HB, 4HB) and PHB, respectively.

The advantage of using PHBV in comparison to PHB is the ease of processing and good toughness. Certain PHBV disadvantages such as low thermal stability and a high degree of crystallinity must be overcome [96]. Improvements, mediated by chemical changes, must be performed together with the preservation of the material's biodegradation property, which, depending on the HV percentage, maybe rigidity or flexibility, similarly to commercial synthetic plastics (polyethylene, polypropylene, and polyvinylchloride), and assurance of biodegradation of the formulated bioplastic [96].

A commercial Ecoflex bioplastic (commercial product of BASF) was compared to PHB and poly (3-hydroxybutyrate-co-3-hydroxyhexanoate) (PHBHHx) in activated sludge for 18 days. Bioplastics composed of PHBHHx showed a higher degree of biodegradability than Ecoflex and PHB, with weight losses of 40, 20, and 5%, respectively [97]. The low crystallinity and morphology of the surface of the bioplastic proved a determining factor in the biodegradation process, observed mainly in bioplastics with 12% HHx (hydroxyhexanoate), which displayed a rough and porous surface before and after undergoing activated exposure to sludge and lipases (Figure 4).

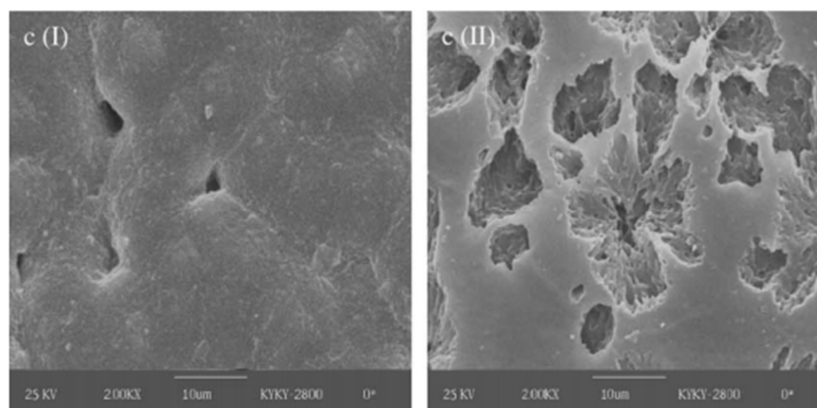


Figure 4. Surface morphology of bioplastic made with PHB (12% HHx) before (left) and after degradation (right) [97].

Besides surface morphology and crystallinity of the bioplastics, other factors, such as mixing components, depth of burial (due to environmental and/or microbial differences), and time of exposure to the soil also determine the biodegradability degree. In the study

performed by Weng et al. [98], evaluating through appearance and fragmentation, the following results were achieved for the biodegradation of polymeric blends (poly (3-hydroxybutyrate-co-4-hydroxybutyrate and poly (lactic acid)—(P (3HB, 4HB)/PLA)): In the first month of testing, blends composed of 100% P (3HB, 4HB) and those with 25% PLA showed loss of integrity (appearance), whereas in the second month, both bioplastics had been almost completely biodegraded. This behavior was similar for the different depths of burial used (20 and 40 cm); however, at 20 cm and 2 months of testing, a greater difficulty was observed in the collection of fragments of blends with 75% of P (3HB, 4HB). For both depths of burial, the higher the concentration of PLA in the blends, the longer the biodegradation time. However, the biodegradation behavior was the opposite for higher concentrations of P (3HB, 4HB).

Polymer blends with 100% and 75% P (3HB, 4HB) were degraded more easily at 20 cm depth, although the presence of PLA in the bioplastics represented a delay in biodegradability at both depths tested. At 40 cm, PLA suffered greater disintegration, due to the anaerobic conditions, providing better conditions for degradation of the PLA, as reported by the authors [98].

In addition to temperature, bioplastic composition, crystallinity, degree of hydrophilicity and environmental conditions in relation to oxygen concentration, another factor that must be taken into account is the abundance of microbial biomass and the efficiency of fungi and bacteria biodegradation in different environments. The biodegradation of microbial polyesters by fungi was reported as dominant in soil [95]. However, the biodegradation of polymers in aquatic (marine) medium was faster with the use of bacteria [99,100].

PHA bioplastics as well as other bioplastics have limitations in their applications and achievements due to the high cost, low mechanical resistance, and impairment of biodegradation in functionalization processes and mixtures with other polymers [93]. In addition to the low ductility property, one of the main disadvantages of using PHAs in the production of bioplastics is the formation of brittle bioplastics, properties that can be improved by mixing biodegradable polymers from oil. However, the sustainability of bioplastic manufacturing is affected since the use of oil in the extraction and refinement stage generates the carbon dioxide production [101]. Another impact that should be considered in the production of PHA bioplastics with synthetic polymers such as the use of PCL is the reduction in the rate of biodegradation [102]. However, the development of polyester bioplastics with bio-based fibers origin (blends development), such as lignocellulosic fibers, can assist in overcoming the low ductility property of bioplastics [93]. This blend reduces costs, ensuring a biodegradable and renewable product.

The application of polyhydroxyalkanoate as a bioplastic has major limitations (e.g., its production costs for replacing conventional plastics [103]). A potential alternative for the optimization of PHA production technologies is the use of organic residues, such as lignocellulosics [104]. As an example, hemicellulose [105–107], cellulose [108] and a mixture of hemicellulose and cellulose hydrolyzate [109] have been used for the production of microbial polyesters, such as PHA and P3HB (PHB). However, the use of lignocellulosic fibers poses limitations mainly related to the production yield and generation of inhibitory substances for PHA-producing microorganisms [104]. Table 1 shows some properties and biodegradation times of different biodegradable bioplastics produced from biopolymers.

Poly(lactic acid) (PLA) is another polyester that may be partially derived from the microbial fermentation of biopolymers. The lactic acid produced by the bacteria is polymerized by a chemical route, thus forming PLA, which offers several advantages, such as rigidity and miscibility with other biodegradable plastics. However, in several application areas (e.g., manufacture of 3D printers), its fibers have been used by Brazilian companies due to the PLA lower heat loss in comparison to oil-derived plastics [110]. Nevertheless, bioplastics from bacterial polyesters should be considered, since PHAs like PBH present several advantages in comparison to PLA [111]. Table 1 shows some properties and biodegradation times of different biodegradable bioplastics produced from biopolymers.

Table 1. Properties and biodegradation time of different biodegradable bioplastics produced from biopolymers.

Bioplastic Type	Polymer Type	CONB	BPR	PAB	TS (MPa)	E (%)	Reference
PHB nanofiber	Polyester	Soil, 30 °C and 80% humidity	100% in 21 days	Weight loss	[112]
PHB/Starch	Polyester	Sludge, 35 °C, anaerobic	93.8% in 190 days	Biogas quantification	[113]
PHB	Polyester	Compost, 55 °C and 70% humidity	Approx. 80% in 28 days	CO ₂ quantification	1015	...	[114]
PHA	Polyester	Seawater	100% in 1.5 to 3.5 years	Literature review	[115]
PHA	Polyester	Soil, 12–15 cm depth and 35% humidity	30% in 60 days	Weight loss	16.2	600.3	[116]
PHA/Rice husk	Polyester/Fibers	Soil, of 12–15 cm depth and 35% humidity	>90% in 60 days	Weight loss	7.5	<400	[116]
PHA	Polyester	Soil, 20 °C and 60% humidity	48.5% in 280 days	CO ₂ quantification	[117]
PHBV/Starch	Polyester/Polysaccharide	Liquid medium	100% in 31 days	CO ₂ quantification	21.01	10.85	[118]
PHBV/NPK	Polyester/Fertilizer	Soil, 25–30 °C and 65% humidity	68.66% in 112 days	Weight loss	[119]
PHBV/Starch	Polyester/ Polysaccharide	Soil, 25 °C and 20% humidity	>60% in 150 days	Weight loss	~7	~3.2	[120]
Starch	Polysaccharide	Soil, 3.5 cm depth and 65% humidity	30% in 5 days	Weight loss	1.88	0.45	[70]
Starch	Polysaccharide	Marine water with sediment	Approx. 69% in 236 days	BOD	4.7 *	211	[121]
Starch	Polysaccharide	Microorganisms in a plate, 25 °C and 75% humidity	100% in 30 days	Weight loss	8.6	52	[69]
Starch/Cellulose	Polysaccharide/Modified	Microorganisms in plate, 25 °C and 75% humidity	100% in 60 days	Weight loss	14.7	50	[69]
Cellulose	Polysaccharide	Soil	100% in 105 days	Weight loss	45	6.1	[68]
Cellulose/Starch	Polysaccharide	Soil/ humus, 25 °C and 75% humidity	24.2 to 39.3% in 35 days	Weight loss	5.6 to 35.0	13.1 to 21.7	[69]
Hemicellulose/ Gelatine	Polysaccharide/Partially hydrolyzed protein	Soil/manure	100% in less than 15 days	Weight loss	[71]
PLA/Starch	Poly(lactic acid)/ Polysaccharide	Compost and 58 °C	79.7% in 90 days	Weight loss	[122]

CONB = Biodegradation conditions; BPR = Biodegradation period and rate; PAB = Biodegradation analysis procedure; TS = Tensile strength; E = elongation; ... = not reported; * = Newton (N).

Bioplastics are renewable and/or biodegradable and display good mechanical properties such as tensile strength similar to certain synthetic plastics in common use (Table 1). Polypropylene and polystyrene, fossil-based synthetic plastics, show TS between 25–40 MPa and 30–55 MPa, respectively [68], whereas it ranges between 55–124 and 9–17 for CellophaneTM and low-density polyethylene (LDPE), respectively [123,124]. This similarity of mechanical properties of bioplastics and plastics was also reported by Hansen et al. [125]. Therefore, even if at present and in the future, the total replacement of non-biodegradable plastic from petroleum, is something unlikely, for some applications, such as bioplastics for use in agriculture (mulch) and packaging (short lifetime), this technology can represent one of the alternatives (along with other actions and technologies) to mitigate the environmental impacts related to plastics.

3.4. Effect of the Bio-Based Polymer Addition on the Biodegradation Rate of PHAs Bioplastics

The addition of bio-based polymers in polyester microbial biocomposites is vast in the literature [93,126,127]. The bio-based polymers application, mainly lignocellulosic fibers, is due to the improvement in the biodegradation rate of the formulated bioplastic [93]. This improvement in the biodegradation of PHAs biocomposite is related to the increase in hydrophilicity and water absorption by bioplastics. A mixture of 30% Sisal fibers (wt) and PHBV resulted in increased water absorption of 14% compared to pure PHBV (0.8%) [128]. The use of Kenaf fibers (main cellulose) in the blend with poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) [P(3HB-co-3HHx)], resulted in a greater loss of mass in biodegradation in soil due to greater water absorption and microbial binding sites in the microbial polyester from binding with Kenaf fiber [129]. This study suggested that the accelerated deterioration of the blend (reduction of mechanical properties), after 6 burial weeks (soil) was due to the weakening of the adhesion between the fiber/[P(3HB-co-3HHx)], with the access of water to the internal hydrophobic regions of the polymer.

The use of hemicellulose with PHAs is also an alternative to increase the blends biodegradation rate in relation to pure microbial polyesters [93]. Bioplastics from PHBV/ Peach Palm Particles (lignocellulosic fiber with considerable hemicellulose content) were biodegraded faster than pure PHBV in soil [130]. The authors reported cracks, corrosion, and discoloration after 2 months of biodegradation. The poor adhesion between the fiber/PHBV interface, which resulted in greater water absorption and accessibility of soil microorganisms, was suggested as contributed to the deterioration.

Starch, another polysaccharide from vegetable biomass, can also be used in the production of bioplastics with reduced biodegradation time. The mixture of starch and PHBV (50/50% wt) was fully biodegraded in the soil after 33 days, i.e., there was a 50% reduction in biodegradation time compared to pure PHBV [131]. The addition of starch reduced the crystallinity of the blend, facilitating the absorption of water by the matrix and increased the enzymatic activity on the surface and in the inner region of the blend. There was an increase in the biodegradation of PHA/starch blends as the starch content increased in the formulation, with biodegradation of PHA/30% starch (wt) corresponding to 44% in 6 months of burial in soil [132].

Chemical modifications of polysaccharides, such as cellulose acetylation (cellulose acetate) can result in partial or total inhibition of blends biodegradation, due to reduced solubilization and hydrophobicity of the fibers. The acetyl and butyryl group in cellulose reduced the rate of biodegradation of the PHB blend/modified cellulose due to the impediment of the substituents and reduced the blends/water interactions [133]. However, in the same study, the mechanical properties were improved by increasing the concentration of cellulose acetate butyrate. Related to cellulose, the degree of substitution above 2.5 results in the inhibition of biodegradation [93]. However, some chemical modifications can positively influence the biodegradation of microbial and bio-based polymer blends. This improvement in biodegradation is due to the increase in the contact area surface of the fibers, resulting from the surface treatments of the fibers, such as, an increase in the

fiber rugosities with the application of NaOH, which removes the hemicellulose and lignin fibers [93].

Lignin is the most recalcitrant constituent of lignocellulosic fibers due to the complexity of the composition of this phenolic macromolecule [82,134]. The lignin enzymatic catalytic degradation needs different enzymes [75,82], or even the synergy of an enzyme complex. The inclusion of lignin in the blends of PHAs and PLA results in steric impediment of the enzyme and reduction of the degree of hydrophilicity, which is shown in the literature as a factor in reducing the biodegradation of polyester blends [93,132]. For example, the biodegradation in soil of the PHA/lignin blend was 4% after 24 weeks, which was lower than the rate of biodegradation of the PHA/10% starch, PHA/cellulose (11.1 and 100% respectively) [132]. An alternative for obtaining bioplastics from microbial polyesters, with guaranteed polymer biodegradability, is the use of enzymes and microorganisms capable of catalyzing the breakdown of lignin. The main enzymes involved in lignin oxidoreduction are laccases (Lac), lignin peroxidase (LiP), and manganese peroxidase (MnP) [82], and the recently discovered enzymes dye-decolorizing peroxidases and unspecific peroxygenase [134,135].

The application of specific microorganisms that degrade lignin and/or PHAs can be an alternative to improve the biodegradation of the blends of these polymers. In nature, these enzymes act synergistically, and some microorganisms can produce the three enzymes, while others only produce a few of the necessary enzymes [82]. LiP has a key role in the degradation of lignin, due to the distinct characteristics of the active site of the enzyme. However, the catalytic action of LiP is mediated by H₂O₂, which is generated by Lac [135]. The effectiveness of the microorganisms is essential for the biodegradation of PHA/lignin blends, as some microorganisms such as *Phanerochaete chrysosporium* are considered excellent for the degradation of lignin [134,136]. However, Brown-rot fungi due to the degradation mechanisms of lignin not being oxidative, presents a reduced degradation process of lignin [82]. Another example is the case of the bacteria *Streptomyces viridosporus*, which can result in a reduced degradation process of lignin since this bacterium acts in the non-phenolic regions of lignin [82,134].

4. Conclusions

Advances in the development of materials and technologies with fewer environmental impacts are highly expected, mainly due to the progress in the area of biopolymers over the past two decades. However, biopolymers application and use in the various sectors of society is limited, i.e., the annual production of bioplastics compared to plastics is still low. In this way, the use of plant biomass and microbial polyesters can help the development of bioplastic feasible, due to the availability of resources, biocompatibility, biodegradability and generally does not result in ecotoxicity. However, the physicochemical and biodegradation properties must be considered for the study of the optimization of bioplastic from natural polymers. Several actions must be taken so that bioplastic can become a reality on a large scale. The state of São Paulo (Brazil) has established a law that prohibits the supply of disposable plastic products to commercial establishments, which may increase the production scale of some bioplastics, thus reducing costs. The approval of a law by the Chinese government that prohibits the import of international plastic wastes for recycling can also encourage the production of bioplastics. An increase in the production and distribution of bioplastics is not sufficient for the development of a more conscious and sustainable society, i.e., care must be taken for the identification of a bioplastic and/or biodegradable material towards no final consumers' mistakes and no unsuitable actions or disposal habits.

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