Bioplastics in the Circular Economy

Subjects: Polymer Science
Contributor: Giulia Infurna

The European Union is working towards the 2050 net-zero emissions goal and tackling the ever-growing environmental and sustainability crisis by implementing the European Green Deal. The shift towards a more sustainable society is intertwined with the production, use, and disposal of plastic in the European economy. Emissions generated by plastic production, plastic waste, littering and leakage in nature, insufficient recycling, are some of the issues addressed by the European Commission. Adoption of bioplastics–plastics that are biodegradable, bio-based, or both–is under assessment as one way to decouple society from the use of fossil resources, and to mitigate specific environmental risks related to plastic waste.

bioplastic | bio-based plastic | biodegradable plastic | bioeconomy | life cycle assessment | sustainability

1. Introduction

The European Green Deal [1] is the action plan outlined by the European Commission (EC) to tackle the ever-growing environment and climate-related challenges our society faces. The plan aims at transforming *"the EU into a fair and prosperous society, with a modern, resource-efficient and competitive economy where there are no net emissions of greenhouse gases in 2050 and where economic growth is decoupled from resource use"* [1] (p. 2). As also stated in its communication *"A new Circular Economy Action Plan for a Cleaner and More Competitive Europe"* [2], the EC underlines the utmost importance of shifting towards a circular economy, with a framework of policies that make sustainable products, services, and business models the norm. On the global scale, The United Nations Development Program (UNDP) also stressed the importance of working towards a sustainable economy, with efficient use of natural resources, little to none waste and pollution [3]. In this context, the EC identifies a series of pressing challenges relating to plastic production, (mis-)use and pollution, spanning from single-use items, over-packaging, and littering, to microplastics, high-carbon footprints, and lack of appropriate labeling. The strategy outlined to tackle these challenges includes supporting the bio-based industry and developing a framework for the use of bio-based plastics, *"based on assessing where the use of bio-based feedstock results in genuine environmental benefits"*, and for the use of biodegradable or compostable plastics, *"based on an assessment of the applications where such use can be beneficial to the environment"* [2] (p. 9). These plastics, which are either bio-based or biodegradable (or both), are referred to as "bioplastics" and have been the topic of much work and discussion at a global level for some time now. The dwindling of fossil resources provides a strong drive to the development of bio-based products, while the possibility to mitigate environmental pollution or simplify organic waste collection are big motivations behind the development of biodegradable and compostable plastic products.

Bioplastics already find applications on the market, particularly as packaging [4][5][6][7], carrier and compost bags [5][6]; they are also applied in the agriculture and horticulture sector [6][8], and in the automotive and electronic industry [6][9]. Furthermore, biodegradable polymers have been long applied in biomedicine [5][10][11]. Still, the production of bio-based plastics is limited to one percent of the worldwide plastic production [7][12] and their adoption comes with uncertainties, as acknowledged in the EC Communication *"A European Strategy for Plastics in a Circular Economy"* [13]. This is exemplified by the research focused on bioplastics sustainability and [8][14][15][16][17][18][19][20][21][22][23][24][25] biodegradability [26][27][28][29][30], as well as the attention of media to the subject. Excluding the ample literature on biomedical applications, academic research has been focusing on the synthesis of bio-based polymers [31][32], on the life cycle assessment (LCA) of the production and end-of-life (EOL) [20][24][33][34] of different bioplastics, and biodegradation under different conditions [10][14][35].

In this paper, we present the reader with an overview of the bioplastics field, including definitions, polymers on the market, and applications. We discuss biotic and abiotic degradation mechanisms and present standards and certifications that are in place to evaluate the compostability and biodegradability of bioplastics. Recent works on the biodegradability of bioplastics are also reviewed. We report on the standards in place for the LCA of bioplastics and review recent studies on the subject, with particular focus on studies that consider the EOL assessment. Finally, given the material reviewed, we concisely discuss the challenges that can be identified with the adoption of bioplastics, as well as possible solutions, and we draw our conclusions on the topic.

1.1. Environmental Impact of Plastics

The generation of plastic waste and subsequent uncontrolled plastic pollution is one of the major environmental problems governments and agencies must face today.

The global production of plastic reached almost 370 million metric tons (Mt) in 2019 [36], almost 60 million of which are produced in Europe. The vast majority of the plastic products that enter the global market are durable materials, in particular, polypropylene and polyethylene are the leading polyolefins on the market, with the production of packaging being the main use of such plastics [36]. As of 2017, it was estimated that 8300 Mt of plastics were produced worldwide while, as of 2015, 79% of all plastic produced had been accumulating in landfills or the environment [37]. The UNEP reports that only 9% of all plastic ever made has been recycled, 12% has been incinerated and the rest accumulates in landfills or nature [38]. Today, 300 Mt of plastic waste are produced every year and around 80% of marine litter is due to plastic debris, with the infamous *"Great Pacific Garbage Patch"* being a dreadful testament to these numbers and with an estimate of 75,000 to 300,000 tons of microplastics entering EU habitats every year [38][39][40][41].

Plastic debris in the natural environment is extremely persistent, with degradation in seawater being estimated from hundreds to thousands of years [42][43]. Plastic marine debris results in severe, harmful, impact on the ecosystem [44]. Because of its long half-life and hydrophobic nature, plastic debris provides excellent conditions for the proliferation of diverse microbial communities, forming an ecosystem referred to as "plastisphere" [45]. The microbial action, together with mechanical stress, thermal and UV-light degradation, results in the fragmentation of the debris into microplastics, to the point that plastic residues can be found in many aquatic species, as well as birds and other wildlife [46]. In turn, this poses a risk to human health by entering the food chain [47][48][49].

A great part of the answer to plastic pollution comes from increasing recycling and repurposing of already produced plastics, as well as replacing several classes of plastic items, particularly single-use products, with recyclable alternatives, and from a change in mentality and habits in our society. At the same time, fossil resources are finite and their use results in greenhouse gas (GHG) emissions. As reported by the Ellen MacArthur Foundation in 2016 [50], it can be estimated that by 2050 the plastics sector *“will account for 20% of total oil consumption and 15% of the global annual carbon budget by 2050 (this is the budget that must be adhered to in order to achieve the internationally accepted goal to remain below a 2 °C increase in global warming)”* [50] (p. 7). The production of plastics from renewable sources has been suggested to achieve a lower carbon footprint, since the raw materials uptake carbon dioxide during their growth, and to alleviate the economy’s dependence on fossil fuel [13][41][50]. The application of biodegradable plastics in specific fields, such as soil cover films, carrier bags, and single-use packaging is also suggested as part of technological advancement in the bioeconomy [7][13].

1.2. Circular Economy and Bioplastics

Broadly speaking, a circular economy is an economic system and production model aimed at maximizing the reuse and recycling of resources, therefore extending the life cycle of products while minimizing waste. The model was thought of as a response to the traditional economy, the linear economy, where resources are used to manufacture products which are then used and discarded as waste. The *Circular Economy Action Plan* presented by the EC in 2020 [2] outlines the main directions towards which the economic model is being developed. We briefly summarize some of the main points made in the document.

Products should be designed with reusability and recyclability in mind, i.e., they need to be more durable, repairable, recyclable. Packaging is to be reduced, restricted to certain applications, and designed for recyclability. The production of single-use items is to be restricted and the destruction of unsold items is to be banned. Finally, more support to the bio-based sector is also considered as one way to enable greater circularity in industry, though it is also noted that the sourcing, labeling and use of bio-based, biodegradable and compostable plastics, are emerging challenges for which the EC will develop a policy framework [2] (p. 9). The topic of bioplastics is more extensively discussed in a 2018 EC action plan [51] focused on bioeconomy.

Overall, the EC communications suggest that the policy will be to support, e.g., via financial and regulatory incentives, the growth of the bioplastics industry, as one way to move towards a low-carbon economy [41][52][53]. For example, more than 100 million euros have been provided to finance R&D focused on alternative feedstocks, as part of the *Horizon 2020 Research Programme* [52]. The European Committee for Standardization (CEN) has also produced several harmonized standards in the past five years, covering methodologies to claim biodegradability and compostability, and to measure the bio-based content of plastics, to better regulate the bioplastic field. Still, it is acknowledged that more standards are required and that applications of biodegradable plastics can come with both positive and negative implications [53].

2. Bioplastics: Definitions and Market

The term bioplastic is often used loosely and synonymously to biodegradable. While some bioplastics are indeed biodegradable, not all are. Bioplastics should be intended as polymers that meet any of two criteria: the polymer is bio-based, the polymer is biodegradable [28][54]. Bio-based means that the polymer is either entirely or partially obtained from biomass, i.e., from any kind of organic renewable material of biological origin as well as organic waste. Biodegradable means that the material can break down into natural substances such as carbon dioxide, water and biomass, due to the action of microorganisms. In a more specific sense, a biodegradable plastic is a plastic material that complies with certain official standards of biodegradability, where a certain amount of degradation needs to be scientifically observed within a certain amount of time and under specific conditions. Similarly, a compostable plastic undergoes biodegradation in industrial composting facilities and has to comply with specific standards.

Bioplastics therefore form three broad groups of polymers: those that are both bio-based and biodegradable, those that are only bio-based and those that are only biodegradable. Some main examples of bioplastics that are both bio-based and biodegradable are polylactic acid (PLA) [55][56], polyhydroxyalkanoates (PHAs) [57] and bio-based polybutylene succinate (bio-PBS) [58], as well as plastics based on starch, cellulose, lignin and chitosan. Examples of bioplastics that are bio-based but not biodegradable are bio-based polyamides (bio-PP), polyethylene (bio-PE), polyethylene terephthalate (bio-PET) [59]. Finally, examples of biodegradable bioplastics that are based on fossil resources are PBS, polycaprolactone (PCL) [60], polyvinyl alcohol (PVA) [61] and polybutylene adipate terephthalate (PBAT) [62]. Furthermore, polymers like bio-PE, which are bio-based and chemically identical to their fossil-based counterparts, are typically referred to as drop-in polymers. Table 1 lists some bioplastics that are frequently encountered on the market or in research, classified on the basis of the origin of the raw materials and their biodegradability.

Table 1. Lists of bioplastics and indication of bio-based origin and biodegradability. In the table, “y” means yes, “n” means no, and “y/n” refers to both statements being valid.

Polymer	Bio-Based	Biodegradable
Polylactic acid (PLA)	y	y
Starch blends, thermoplastic starch (TS)	y	y
Polyhydroxyalkanoates (PHAs)	y	y
Polybutylene succinate (PBS)	y/n	y
Polyurethanes (PURs)	y/n	y/n
Polycaprolactone (PCL)	n	y

Polymer	Bio-Based	Biodegradable
Polyvinyl alcohol (PVA)	n	y
Polybutylene adipate terephthalate (PBAT)	n	y
Polyethylene Furanoate (PEF)	y	n
Bio-polypropylene (bio-PP)	y	n
Polytrimethylene terephthalate (PTT)	y	n
Bio-polyethylene terephthalate (bio-PET)	y	n
Bio-polyethylene (bio-PE)	y	n
Bio-polyamides (bio-PAs)	y	n

Today's production volume of bioplastics is relatively small when compared to the numbers of the common plastic industry. According to European Bioplastics, the global production of bioplastics in 2018 was around 2 Mt [12], while the global production for plastics was around 360 Mt. At the same time it is anticipated that the global market for bioplastics will grow steadily for the next five year, increasing in volume by around 40% [12]. Different examples of bioplastics already exist on the market and are produced by companies both in Europe, the USA and Asia, with some of the most important manufacturer being BASF (Germany), Corbion N.V. (Netherlands), NatureWorks LLC (USA), CJ CheilJedang (Korea), Novamont (Italy), Tianjin Guoyun (China). Two historically successful examples are Cellophane™, produced from regenerated cellulose by Futamura Chemical Company (UK), and Nylon-11 produced from castor oil by different manufacturers. More examples are the PLA branded Ingeo™ produced by NatureWorks LLC, as well as the Luminy® series of PLA resins produced by Total Corbion (fifty-fifty joint venture between Total and Corbion), which is also working on the production of bio-based PEF; Corbion distributes its PURASORB® grades of bioresorbable polymers, which include PLA, PCL and copolymers; Danimer Scientific produces the PHA-based bioplastic Nodax™; several compostable polymers are produced by BASF (ecoflex®, ecovio®); Novamont produces its biodegradable, starch-based, Mater-Bi™; Arkema produces a series of bio-PA (Nylon) under the name Rilsan®.

2.1. Production Routes of Bio-Based Plastics and Main Examples

As already introduced, bio-based plastics are entirely or partially obtained from some type of biological source, this includes plants, microorganisms, algae, as well as food waste. Some bio-based plastics are obtained from polymers that form directly in nature, within microorganisms and plants. Notably, cellulose—the most abundant organic compound and the main constituent in plant fibers—has been used ever since the 19th century. Other bio-based plastics are relatively novel and are obtained through synthetic routes making use of natural resources to formulate monomers which are then polymerized. In general, we can identify three main routes to produce bio-based plastics: (1) polymerization of bio-based monomers; (2) modification of naturally occurring polymers; (3) extraction of polymers from microorganisms. Table 2 lists some of the main bio-based polymers grouped by their production route and followed by a brief description of their synthesis.

Table 2. List of common bio-based polymers and overview of their production.

Polymer	Technology Overview	Route
Polylactic acid	Fermentation of carbohydrates (e.g., starch) yields lactic acid which polymerizes to low M_n PLA. This depolymerizes to lactide, which polymerizes to high M_n PLA.	1
Polybutylene succinate	Bacterial fermentation of carbohydrates yields succinic acid, which is esterified to also obtain 1,4-butanediol. The two chemicals polymerize to PBS.	
Polyurethanes	Polyols obtained from plant oils are reacted with isocyanates or bio-isocyanates to yield PURs.	
Polyamides	Diacids derived from castor oil are reacted with a diamine to yield PAs. A typical pair is sebacic acid and decamethylenediamine (obtained from the acid).	
Polyethylene	Fermentation of saccharides yields bioethanol, then dehydrated to ethylene. Polymerization yields bio-PE.	
Thermoplastic starch	Typically obtained by gelatinization of starch (from corn, cassava, etc.) followed by casting or by extrusion of starch pellets and plasticizers.	2
Cellulose acetate	Cellulose from wood pulp is converted to a triacetate form which is then hydrolyzed to cellulose acetate.	
Regenerated cellulose	Cellulose is converted to a soluble form, then regenerated to obtain a film (cellophane) or a fiber (rayon).	
Polyhydroxyalkanoates	Intracellularly accumulated by different bacteria. Polyhydroxybutyrate was the first to be discovered.	3

Today, several bio-based polymers are produced through the polymerization of monomers obtained from natural sources, PLA being the primary example. Polylactic acid is a thermoplastic aliphatic polyester obtained from the fermentation of plant-derived carbohydrates, e.g., sugars obtained from sugarcane or sugar beet, or starch obtained from corn or potato. The fermentation process makes use of various microorganisms, typically *Lactobacilli* strains, which convert sugars to lactic acid [55][63]. If starch is used as feedstock, this is first enzymatically converted to sugars (glucose). Most commonly, the lactic acid is then polymerized to low molecular weight (Mn) PLA oligomers, which are in turn depolymerized to yield lactide, the cyclic dimer of PLA. The ring-opening polymerization (ROP) of lactide will then yield high Mn PLA [55][64][65]. Due to the chiral nature of the monomers, L(-) and D(+), in use during the polymerization process, three stereochemical forms of PLA can be obtained. Depending on the ratio of L- to D-isomers, the resulting polymer can be amorphous or show different degree of crystallinity, with influence on degradation [66] and mechanical properties [67]. PLA processability is comparable to many commodity thermoplastics, which leads to its use as packaging material [56][68]. PLA is also recognized as biodegradable and compostable [55][64][65], it is therefore used in the production of compost bags and disposable tableware, and other applications where recovery of the used product is not feasible. Furthermore, PLA biocompatibility has made it into one of the most important polymers in biomedicine and tissue engineering [55][64][65][69]. Finally, PLA is one of the main materials in use to produce filaments for fused deposition modeling, a common 3D printing manufacturing process [70].

PBS is another thermoplastic polyester that can be produced from the microbial fermentation of sugars derived from natural feedstocks. The typical route of production for PBS is the esterification of succinic acid with 1,4-butanediol [71], where the succinic acid can be obtained from the anaerobic fermentation of bacteria or yeast and subsequently reduced to 1,4-butanediol. Several microorganisms have been studied for the biosynthesis of succinic acid, e.g., *Anaerobiospirillum succiniciproducens* and *Actinobacillus succinogenes* [72]. The polymerization process proceeds through a first step during which the 1,4-butanediol is reacted with the succinic acid to yield oligomers of PBS, and a second step of polycondensation of the oligomers to yield semicrystalline, high M_n PBS [58]. PBS shows similar properties to polyethylene terephthalate and polypropylene and finds applications as compostable packaging and bags, as mulch film and hygiene products [58][73]. The use of PBS in biomedical applications has also been attracting significant attention, thanks to its biodegradability and low toxicity profile, though its low flexibility and slow degradability rate need to be circumvented by blending or copolymerization with other polymers, such as PLA [71][73].

Bio-based polyethylene is an aliphatic thermoplastic synthesized from the polymerization of bioethanol. The bioethanol is obtained through the fermentation of sugars from the aforementioned feedstocks (sugarcane, sugar beet, and starch from corn, wheat or potato) [59], yeast or bacteria being used as fermentation agents [74]. The bioethanol is distilled and dehydrated to obtain ethylene which is then polymerized to bio-PE. The polymer is equivalent to fossil-derived polyethylene and the same different types (low and high density, linear and branched) can be obtained, consequently, bio-PE can be used for any of the many applications of PE. It should also be noted that bioethanol can also be used in the synthesis of other important plastics such as polyvinyl chloride, polystyrene and polyethylene terephthalate [59].

Several naturally occurring polymers can be used to produce bio-based and biodegradable plastics, in particular the polysaccharides starch and cellulose.

Among naturally occurring polymers, cellulose is the most abundant one, being ubiquitous in plants. It is a structural polysaccharide based on repeating units of D-glucose. Cellulose has attracted great attention from research and industry due to its abundance, low-cost, biocompatibility and biodegradability. Cellulose is typically obtained from wood through a pulping process and can be converted to different materials, in particular two main cellulose-based plastics (or cellulosics) are regenerated cellulose and cellulose diacetates [75]. In the production of cellulose diacetates, the cellulose is first converted to cellulose triacetate by reaction with acetic anhydride, this is then partially hydrolyzed to obtain a lower degree of substitution. Most typically cellulose diacetates are produced with degree of substitution around 2.5. Cellulose acetates find several applications in the textile industry [76], as fibers in cigarette filters [77], films (e.g., photography) and membranes in separation technologies (e.g., hemodialysis) [78]; manufactured as porous beads they have potential applications in biomedicine and biotechnology [79]. Cellulose diacetate is also biodegradable under different natural conditions with the process being accelerated by hydrolysis [80].

Regenerated cellulose is typically prepared following the viscose process (though other industrial methods exist), in which cellulose is converted to cellulose xanthogenate by reaction with alkali and carbon disulfide. The intermediate is dissolved in NaOH solutions, resulting in a mixture called viscose, which can be processed as films and fibers and treated in acidic solutions to yield regenerated cellulose [81][82]. Regenerated cellulose materials are either already applied or could find applications, in different fields, from textile and packaging, to biotechnology and biomedicine [82]. Rayon and cellophane, which are generic trademarks for regenerated cellulose fibers and films respectively, are materials with great commercial importance. Rayon finds many applications in the textile industry, from the manufacture of clothing to the production of wound dressings [83]. Cellophane is almost ubiquitous in the food packaging market, but also in the cosmetic (casing, boxes, etc.) and pharmaceutical industry [82].

Starch-based polymers form an important family of bioplastics on the market. Starch is a polysaccharide consisting of two main macromolecules, amylose and amylopectin, and is obtained from feedstocks such as corn, rice, wheat or potato [84][85]. Thermoplastic starch (TPS) is the material obtained from a granular form of native starch, through thermomechanical processing (extrusion) with the addition of gelatinization agents or plasticizers [84][85][86][87]. Typical plasticizers in use to improve the processability of TPS are glycerol and other polyols, sugars, amides and amines, and citric acid [84]. TPS can be used on its own, though very often it is used as part of polymeric blends with polymers such as PLA and other polyesters, to improve its properties. Starch-based plastics find different applications in the packaging, food, textile and pharmaceutical industry [88][89][90].

Bacteria can synthesize and accumulate a large number of biopolymers, many of which can be potentially exploited for industrial applications or as high-value products in the medical field [91]. Polyhydroxyalkanoates are a family of polyesters synthesized by the activity of several types of bacteria, where they accumulate serving the purpose of carbon reserve material. The intracellular accumulation of PHAs is typically promoted by particular culturing conditions and nutrients starvation, which can lead to high concentration of accumulated polymer [71][91][92][93][94]. Several renewable feedstocks, as well as carbon dioxide, chemicals and fossil resources, can be used as substrate for the production of PHAs [94]. In a typical process a seed culture containing the chosen bacteria is inoculated in a fermentation vessel containing the fermentation medium. At the end of the culturing period, the polymers can be obtained by solvent extraction, separated from the residual biomass and reprecipitated by mixing with a non-solvent, typically an alcohol [31][71][95]. To this day, more than 150 monomeric units have been identified, which can lead to different polymers with different properties. Polyhydroxybutyrate (PHB) is the simplest PHA and the first one to be discovered in the bacterium *Bacillus megaterium*. PHAs find applications in the packaging, food and chemical industry, though most recently attention has been shifting towards possible agricultural and medical applications [96][97][98].

2.2. Biodegradability and Compostability Standards

As introduced, biodegradable polymers are susceptible to be broken down into simple compounds because of microbial action. Many plastics have been known to undergo this process in a reasonably short time (e.g., six months), and are commonly identified as biodegradable, though to substantiate biodegradability claims, certain standards have been put into place in the past twenty years. These standards present methodologies to evaluate the biodegradability and compostability of a plastic, where compostable refers to the material being degraded under specifically designed conditions and by specific microorganisms, typically in industrial composting facilities. The main standardization bodies involved are the International Organization for Standardization (ISO), European Committee for Standardisation (CEN) and the American Society for Testing and Materials (ASTM). Table 3 reports the main ISO [99] and CEN [100] standards in place, many of which are shared as the CEN standards are often based on the ISO ones. In particular, for a polymer to be marketed as biodegradable or compostable the main standards to conform to are the European EN 13432 or EN 14995 or the international ISO 17088 (other equivalents would be the USA ASTM 6400 or the Australian AS4736). As part of the requirements to pass the standards, the testing methodologies in use to evaluate biodegradability need to be the ones outlined by other official standards, for example EN ISO 14855. The simulated environment, the biodegradability indicator in use, the inoculum in use, test duration, number of replicates required and percentage of evaluated biodegradability to pass the test, are focus points for biodegradability testing standards. It can be noticed that the biodegradability evaluation is carried out by different experimental methodologies, such as release of carbon dioxide and oxygen demand measurements. Indeed, the main indicators of biodegradation adopted by these standards are the measurement of BOD (the biological oxygen demand) or the measurement of evolved CO_2, though also mass loss measurements, measurements of CH_4 evolution, as well as surface morphology and spectroscopy analysis are methodologies in use [101]. Biodegradability standards describe a series of well-defined conditions under which biodegradability or compostability tests are to be carried out, for example temperature, microbial activity and humidity. While this is required for reproducibility and repeatability of results, researchers have pointed out the difficulty in encompassing the variability of conditions encountered in natural, open environments [10][14]. In particular, the more environmentally harmful perspective of plastic waste leaking into the natural environment leads to a series of possible environmental conditions that are hard to accurately predict and simulate. For example, plastic debris leaked in the sea is exposed to a wide range of temperatures, depending on climate, biomes, buoyancy, and other characteristics that might very well change over time. Given that the appeal of biodegradable plastics in several applications is their supposed ability to degrade in the environment, completely and harmlessly, it is of utmost importance to understand the validity of these standards outside of laboratory conditions. In a 2018 review of biodegradability standards, Harrison et al. [35] found that the international standards in use would be insufficient to predict the biodegradability of carrier bags in aqueous environments (wastewater, marine and inland waters). They concluded that the standards in use would typically underestimate the time required for polymers to undergo biodegradation in a natural, uncontrolled environment, particularly because of the methods in use relying on artificially modified media and inocula and relatively high temperatures, that do not reflect what is commonly expected in a natural environment. In 2017, Briassoulis et al. [102] come to similar conclusions when reviewing the standards relevant to the biodegradability of plastics in soil, particularly for the agriculture and horticulture environment. They observe that the standard methodologies enhance the conditions for biodegradation of the specimens in a way that may not be representative of the natural environment, where temperature, water content and soil properties can vary considerably. The standards caution the users about the potential difference between laboratory and natural environment results, though it is not clear how the methodologies should be modified to obtain more representative conclusions. In a 2017 work, Emadian et al. [103] reviewed a series of studies on the biodegradation of bioplastics in different conditions. For the same biopolymers, they reported extremely different results across the studies taken into consideration. For example, testing the biodegradability of PLA in compost researchers reported biodegradation values as low as 13% over 60 days [104] and as high as 70% over 28 days [105]. This difference in results is due to different methodologies, conditions and sample geometry and size being in use, and therefore stresses the need for standard procedures being followed during laboratory tests. Though, at the same time, the kind of differences that create this discrepancy, can also be encountered in a natural environment, and further stress the problem of how well biodegradability can be predicted outside of a laboratory. Further problematics can be encountered when considering the biodegradation of polymeric blends instead of homopolymers. In a 2018 paper Narancic et al. [14] reported on the biodegradability of several biopolymers and their blends in different environments, following the relative standards. The paper is extremely thorough, and its full analysis goes beyond the scope of this review, though one conclusion was that the polymeric blends would generally biodegrade well under industrial composting conditions, but they would show poor biodegradation in aquatic environment and soil. Interestingly, the authors observed that, while PLA is generally not home-compostable, when blended with PCL it would result in a material that could undergo biodegradation under home-composting conditions (though not in soil). At the same time, this was not the case for blends of PLA and PHB, which remained not home-compostable.

Table 3. Main ISO and CEN standards relating to biodegradability and compostability of plastics.

Standard	Title
EN ISO 10210:2017	Plastics—Methods for the preparation of samples for biodegradation testing of plastic materials (ISO 10210:2012)
EN 14995:2006	Plastics—Evaluation of compostability—Test scheme and specifications
EN 13432:2000	Packaging—Requirements for packaging recoverable through composting and biodegradation—Test scheme and evaluation criteria for the final acceptance of packaging
EN 14046:2003	Packaging—Evaluation of the ultimate aerobic biodegradability of packaging materials under controlled composting conditions—Method by analysis of released carbon dioxide
EN 17033:2018	Plastics—Biodegradable mulch films for use in agriculture and horticulture—Requirements and test methods
ISO 17088:2012	Specifications for compostable plastics
EN ISO 14855-1:2012 EN ISO 14855-2:2018	Determination of the ultimate aerobic biodegradability of plastic materials under controlled composting conditions—Method by analysis of evolved carbon dioxide—Part 1: General method (ISO 14855-1:2012)—Part 2: Gravimetric measurement of carbon dioxide evolved in a laboratory-scale test (ISO 14855-2:2018)
EN ISO 16929:2019	Plastics—Determination of the degree of disintegration of plastic materials under defined composting conditions in a pilot-scale test (ISO 16929:2019)

Standard	Title
EN ISO 20200:2015	Plastics—Determination of the degree of disintegration of plastic materials under simulated composting conditions in a laboratory-scale test (ISO 20200:2015)
ISO 23977-1:2020 ISO 23977-2:2020	Plastics—Determination of the aerobic biodegradation of plastic materials exposed to seawater—Part 1: Method by analysis of evolved carbon dioxide—Part 2: Method by measuring the oxygen demand in closed respirometer
EN ISO 14853:2017	Plastics—Determination of the ultimate anaerobic biodegradation of plastic materials in an aqueous system—Method by measurement of biogas production (ISO 14853:2016)
EN ISO 14851:2019	Determination of the ultimate aerobic biodegradability of plastic materials in an aqueous medium—Method by measuring the oxygen demand in a closed respirometer (ISO 14851:2019)
EN ISO 14852:2018	Determination of the ultimate aerobic biodegradability of plastic materials in an aqueous medium—Method by analysis of evolved carbon dioxide (ISO 14852:2018)
EN 17417:2020	Determination of the ultimate biodegradation of plastics materials in an aqueous system under anoxic (denitrifying) conditions—Method by measurement of pressure increase
EN ISO 10634:2018	Water quality—Preparation and treatment of poorly water-soluble organic compounds for the subsequent evaluation of their biodegradability in an aqueous medium (ISO 10634:2018)
EN ISO 14593:2005	Water quality—Evaluation of ultimate aerobic biodegradability of organic compounds in aqueous medium—Method by analysis of inorganic carbon in sealed vessels (CO_2 headspace test) (ISO 14593:1999)
EN ISO 11733:2004	Water quality—Determination of the elimination and biodegradability of organic compounds in an aqueous medium—Activated sludge simulation test (ISO 11733:2004)
EN ISO 17556:2019	Plastics—Determination of the ultimate aerobic biodegradability of plastic materials in soil by measuring the oxygen demand in a respirometer or the amount of carbon dioxide evolved (ISO 17556:2019)
EN ISO 11266:2020	Soil quality—Guidance on laboratory testing for biodegradation of organic chemicals in soil under aerobic conditions (ISO 11266:1994)
EN ISO 15985:2017	Plastics—Determination of the ultimate anaerobic biodegradation under high-solids anaerobic-digestion conditions—Method by analysis of released biogas (ISO 15985:2014)
EN ISO 18830:2017	Plastics—Determination of aerobic biodegradation of non-floating plastic materials in a seawater/sandy sediment interface—Method by measuring the oxygen demand in closed respirometer (ISO 18830:2016)
EN ISO 19679:2020	Plastics—Determination of aerobic biodegradation of non-floating plastic materials in a seawater/sediment interface—Method by analysis of evolved carbon dioxide (ISO 19679:2020)

Standard	Title
ISO 13975:2019	Plastics—Determination of the ultimate anaerobic biodegradation of plastic materials in controlled slurry digestion systems—Method by measurement of biogas production
ISO 22404:2019	Plastics—Determination of the aerobic biodegradation of non-floating materials exposed to marine sediment—Method by analysis of evolved carbon dioxide
ISO/DIS 23517-1 (under development)	Plastics—Biodegradable mulch films for use in agriculture and horticulture Part 1: Requirements and test methods regarding biodegradation, ecotoxicity and control of constituents

Figure 1 ıstria and ·cribed by heme for Industrial rtification. Soil biodegradability is also certified by two of the labels through EN 17033, which therefore limits the certification to mulch film. Two labels for biodegradability in water are offered by TÜV but they are independent from EN standards.

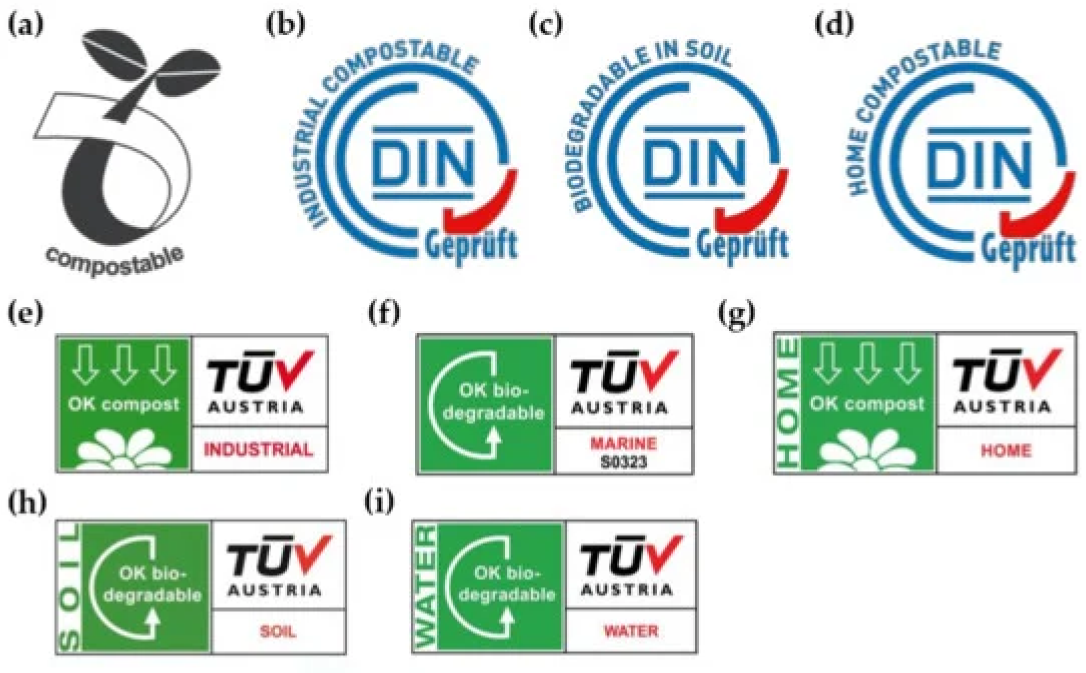

Figure 1. Certification labels relating to biodegradability and compostability: (**a**) seedling logo by *European Bioplastics*, indicates that the product is industrially compostable and complies with EN 13432; (**b**–**d**) DIN CERTCO labels for industrial compostability, biodegradability in soil and home compostability, respectively; (**e**–**i**) TÜV Austria labels for industrial compostability, marine biodegradability, home compostability, soil biodegradability and freshwater biodegradability, respectively.

2.3. Overview of Abiotic and Biotic Degradation Mechanisms

While the official definition of biodegradation is exclusively focused on the biotic phenomena, it is important to remember that abiotic phenomena take place during the biodegradation of a polymeric material, and these can have a strong influence on the overall degradation rate. We can identify three main steps through which biodegradation proceeds, with the process being susceptible to stop at each step [103][106][107][108].

During a first step referred to as biodeterioration, the material is broken down into smaller fractions due to biotic and abiotic activity. During this step a biofilm is formed on the surface of the material, consisting of a variety of microorganisms embedded in a matrix of water, proteins and polysaccharides produced by the same microorganisms [109][110]. The process of colonization of a polymeric surface by a microbial biofilm is referred to as fouling and follows different steps that lead to the settlement of bacteria and other microorganisms (microfouling) as well as larger organisms (macrofouling) such as larvae [110][111]. During and subsequently the biofilm formation, the microorganisms can infiltrate the surface porosity of the polymer which results in a change of the porous volume and potentially in cracks, furthermore this process facilitates water infiltration and consequentially hydrolysis. Additives and plasticizers can also leach out of the polymer during this step, resulting in embrittlement and rupture.

The microorganisms inhabiting the biofilm secrete enzymes that can be broadly defined as intracellular and extracellular depolymerase [28][101][103][106][110]. These enzymes are responsible for the second step in biodegradation, the depolymerization step, during which the polymer chains are broken down into shorter oligomers and eventually monomers, though this process can also result from abiotic phenomena which are covered later in this section.

The third step of biodegradation comprises of the assimilation and mineralization processes during which monomers and oligomers from the broken-down polymer can reach the cytoplasm and enter the metabolism of the microorganisms, therefore being converted to metabolites, energy and biomass, with the release in the environment gases, organic compounds and salts [106]. This step is of particular importance given that several standardized methodologies rely on the analysis of evolved CO_2 to evaluate biodegradability.

Abiotic degradation phenomena are involved either before or in concomitance with biotic degradation. Typical abiotic degradation phenomena are mechanical, thermal, UV, and chemical degradation.

Mechanical damage, both at macro and microscopical scale, can facilitate and accelerate other types of abiotic and biotic degradation, for example by increasing the available contact surface or creating defects that are easily attacked by chemical infiltration and more susceptible to heat damage.

Heat can further increase mechanical damage by lowering the mechanical properties of the polymer, e.g., if the plastic were to experience temperatures higher than its glass transition or melting temperature, its structural integrity would be quickly compromised under relatively low forces. Conversely, temperatures much lower than the glass transition might result in brittleness and rupture of the polymer. The loss of crystallinity, as well as the transition to the rubbery state, can also increase the permeability of biotic and abiotic agents in the polymeric matrix, therefore accelerating the degradation process. This is particularly important for polyesters, such as PLA, where the degradation process is strongly governed by hydrolysis reactions and therefore will proceed at a much faster rate when water can easily penetrate the polymeric network.

Chemical degradation includes oxidative phenomena due to molecular oxygen and is, therefore, one of the main factors in abiotic degradation. Oxidation often proceeds concomitantly with light degradation phenomena, leading to the formation of free radicals, ultimately decreasing the molecular weight by chain scission as well as causing crosslinking of the polymeric network which often leads to high brittleness. Hydrolysis is the other main factor acting during chemical degradation. Several bioplastics contain hydrolyzable covalent bonds, e.g., ester, ether, carbamide groups. Chemical degradation acts synergistically with all other degradation mechanisms. For example, oxidation and hydrolysis are facilitated by the polymer transitioning to the rubbery state and additionally losing its crystallinity due to exposure to relatively high temperatures.

UV-light degradation, or photodegradation, is also a very common occurrence in everyday life plastics. Photodegradation can typically lead to radicalization, resulting in chain scission and/or crosslinking, as already discussed these phenomena can be concomitant to oxidative degradation. Typically, photodegradation will result in the plastic material break down, which in turn increases the surface area available for biotic degradation to occur, and ultimately speeding up the biodegradation process. It can therefore be expected a large difference in biodegradation times depending on the plastic debris being exposed to sunlight or less; this could be the difference between a plastic bag floating at the sea surface against dense plastic debris sinking to deep-sea level.

References

1. European Commission. The European Green Deal COM(2019) 640 Final; European Commission: Brussels, Belgium, 2019.
2. European Commission. A New Circular Economy Action Plan For a Cleaner and More Competitive Europe COM(2020) 98 Final; European Commission: Brussels, Belgium, 2020.
3. United Nations Sustainable Development Knowledge Platform the 2030 Agenda for Sustainable Development. Available online: (accessed on 5 April 2021).
4. Peelman, N.; Ragaert, P.; De Meulenaer, B.; Adons, D.; Peeters, R.; Cardon, L.; Van Impe, F.; Devlieghere, F. Application of bioplastics for food packaging. Trends Food Sci. Technol. 2013, 32, 128–141.
5. Pilla, S. (Ed.) Handbook of Bioplastics and Biocomposites Engineering Applications; John Wiley & Sons, Inc.: Hoboken, NJ, USA, 2011; ISBN 9781118203699.
6. George, A.; Sanjay, M.R.; Srisuk, R.; Parameswaranpillai, J.; Siengchin, S. A comprehensive review on chemical properties and applications of biopolymers and their composites. Int. J. Biol. Macromol. 2020, 154, 329–338.
7. European Environment Agency. The Circular Economy and the Bioeconomy—Partners in Sustainability; European Environment Agency: Copenhagen, Denmark, 2018; ISBN 9789292139742.

8. Razza, F.; Briani, C.; Breton, T.; Marazza, D. Metrics for quantifying the circularity of bioplastics: The case of bio-based and biodegradable mulch films. Resour. Conserv. Recycl. 2020, 159.
9. Barillari, F.; Chini, F. Biopolymers—Sustainability for the Automotive Value-added Chain. ATZ Worldw. 2020, 122, 36–39.
10. Narancic, T.; Cerrone, F.; Beagan, N.; O’Connor, K.E. Recent advances in bioplastics: Application and biodegradation. Polymers 2020, 12, 920.
11. Kaplan, D.L. Introduction to Biopolymers from Renewable Resources. In Biopolymers from Renewable Resources; Springer: Berlin/Heidelberg, Germany, 1998; pp. 1–29.
12. European Bioplastics. Bioplastics Market. Available online: (accessed on 1 November 2020).
13. European Commission. A European Strategy for Plastics in a Circular Economy COM(2018) 28 Final; European Commission: Brussels, Belgium, 2018.
14. Narancic, T.; Verstichel, S.; Reddy Chaganti, S.; Morales-Gamez, L.; Kenny, S.T.; De Wilde, B.; Babu Padamati, R.; O’Connor, K.E. Biodegradable Plastic Blends Create New Possibilities for End-of-Life Management of Plastics but They Are Not a Panacea for Plastic Pollution. Environ. Sci. Technol. 2018, 52, 10441–10452.
15. Shen, L.; Worrell, E.; Patel, M.K. Open-loop recycling: A LCA case study of PET bottle-to-fibre recycling. Resour. Conserv. Recycl. 2010, 55, 34–52.
16. Zhu, Y.; Romain, C.; Williams, C.K. Sustainable polymers from renewable resources. Nature 2016, 540, 354–362.
17. Kawasaki, J.; Silalertruksa, T.; Scheyvens, H.; Yamanoshita, M. Environmental sustainability and climate benefits of green technology for bioethanol production in Thailand. J. Int. Soc. Southeast Asian Agric. Sci. 2015, 21, 78–95.
18. Brizga, J.; Hubacek, K.; Feng, K. The Unintended Side Effects of Bioplastics: Carbon, Land, and Water Footprints. One Earth 2020, 3, 45–53.
19. Yates, M.R.; Barlow, C.Y. Life cycle assessments of biodegradable, commercial biopolymers—A critical review. Resour. Conserv. Recycl. 2013, 78, 54–66.
20. Spierling, S.; Knüpffer, E.; Behnsen, H.; Mudersbach, M.; Krieg, H.; Springer, S.; Albrecht, S.; Herrmann, C.; Endres, H.J. Bio-based plastics—A review of environmental, social and economic impact assessments. J. Clean. Prod. 2018, 185, 476–491.
21. Matsuura, E.; Ye, Y.; He, X. Sustainability opportunities and challenges of bioplastics. Master Thesis, School of Engineering, Blekinge Institute of Technology, Karlskrona, Sweden, 2008.
22. Hottle, T.A.; Bilec, M.M.; Landis, A.E. Sustainability assessments of bio-based polymers. Polym. Degrad. Stab. 2013, 98, 1898–1907.

23. Álvarez-Chávez, C.R.; Edwards, S.; Moure-Eraso, R.; Geiser, K. Sustainability of bio-based plastics: General comparative analysis and recommendations for improvement. J. Clean. Prod. 2012, 23, 47–56.
24. Hottle, T.A.; Bilec, M.M.; Landis, A.E. Biopolymer production and end of life comparisons using life cycle assessment. Resour. Conserv. Recycl. 2017, 122, 295–306.
25. Bisinella, V.; Albizzati, P.F.; Astrup, T.F.; Damgaard, A. Life Cycle Assessment of Grocery Carrier Bags; Danish Environmental Protection Agency: Copenhagen, Denmark, 2018; pp. 1–144.
26. Rutkowska, M.; Krasowska, K.; Heimowska, A.; Steinka, I.; Janik, H. Degradation of polyurethanes in sea water. Polym. Degrad. Stab. 2002, 76, 233–239.
27. Saygin, H.; Baysal, A. Degradation of subμ-sized bioplastics by clinically important bacteria under sediment and seawater conditions: Impact on the bacteria responses. J. Environ. Sci. Health Part A 2020, 56, 1–12.
28. Tokiwa, Y.; Calabia, B.P.; Ugwu, C.U.; Aiba, S. Biodegradability of plastics. Int. J. Mol. Sci. 2009, 10, 3722–3742.
29. Kale, G.; Auras, R.; Singh, S.P.; Narayan, R. Biodegradability of polylactide bottles in real and simulated composting conditions. Polym. Test. 2007, 26, 1049–1061.
30. Accinelli, C.; Saccà, M.L.; Mencarelli, M.; Vicari, A. Deterioration of bioplastic carrier bags in the environment and assessment of a new recycling alternative. Chemosphere 2012, 89, 136–143.
31. Babu, R.P.; O'Connor, K.; Seeram, R. Current progress on bio-based polymers and their future trends. Prog. Biomater. 2013, 2, 8.
32. Nakajima, H.; Dijkstra, P.; Loos, K. The Recent Developments in Biobased Polymers toward General and Engineering Applications: Polymers that are Upgraded from Biodegradable Polymers, Analogous to Petroleum-Derived Polymers, and Newly Developed. Polymers 2017, 9, 523.
33. Walker, S.; Rothman, R. Life cycle assessment of bio-based and fossil-based plastic: A review. J. Clean. Prod. 2020, 261, 121158.
34. Bishop, G.; Styles, D.; Lens, P.N.L. Environmental performance comparison of bioplastics and petrochemical plastics: A review of life cycle assessment (LCA) methodological decisions. Resour. Conserv. Recycl. 2021, 168, 105451.
35. Harrison, J.P.; Boardman, C.; O'Callaghan, K.; Delort, A.-M.; Song, J. Biodegradability standards for carrier bags and plastic films in aquatic environments: A critical review. R. Soc. Open Sci. 2018, 5, 171792.
36. PlasticsEurope Plastics—The Facts. 2020. pp. 1–64. Available online: (accessed on 1 November 2020).

37. Geyer, R.; Jambeck, J.R.; Law, K.L. Production, use, and fate of all plastics ever made. Sci. Adv. 2017, 3, 25–29.
38. UNEP Web Page—Beat Plastic Pollution. Available online: (accessed on 1 November 2020).
39. European Commission. Proposal for a Directive of the European Parliament and of the Council: On the Reduction of the Impact of Certain Plastic Products on the Environment COM(2018) 340 Final; European Commission: Brussels, Belgium, 2018.
40. Lebreton, L.; Slat, B.; Ferrari, F.; Sainte-Rose, B.; Aitken, J.; Marthouse, R.; Hajbane, S.; Cunsolo, S.; Schwarz, A.; Levivier, A.; et al. Evidence that the Great Pacific Garbage Patch is rapidly accumulating plastic. Sci. Rep. 2018, 8, 4666.
41. European Commission. A Circular Economy for Plastics—Insights from Research and Innovation to Inform Policy and Funding Decisions; European Commission: Brussels, Belgium, 2019; ISBN 9789279984297.
42. Gallo, F.; Fossi, C.; Weber, R.; Santillo, D.; Sousa, J.; Ingram, I.; Nadal, A.; Romano, D. Marine litter plastics and microplastics and their toxic chemicals components: The need for urgent preventive measures. Environ. Sci. Eur. 2018, 30, 13.
43. UNEP. Marine Litter Vital Graphics; UNEP: Nairobi, Kenya, 2016; ISBN 9788277011530.
44. Gregory, M.R. Environmental implications of plastic debris in marine settings—Entanglement, ingestion, smothering, hangers-on, hitch-hiking and alien invasions. Philos. Trans. R. Soc. B Biol. Sci. 2009, 364, 2013–2025.
45. Zettler, E.R.; Mincer, T.J.; Amaral-Zettler, L.A. Life in the “plastisphere”: Microbial communities on plastic marine debris. Environ. Sci. Technol. 2013, 47, 7137–7146.
46. Andrady, A.L. Microplastics in the marine environment. Mar. Pollut. Bull. 2011, 62, 1596–1605.
47. Rochman, C.M.; Tahir, A.; Williams, S.L.; Baxa, D.V.; Lam, R.; Miller, J.T.; Teh, F.-C.; Werorilangi, S.; Teh, S.J. Anthropogenic debris in seafood: Plastic debris and fibers from textiles in fish and bivalves sold for human consumption. Sci. Rep. 2015, 5, 14340.
48. Smith, M.; Love, D.C.; Rochman, C.M.; Neff, R.A. Microplastics in Seafood and the Implications for Human Health. Curr. Environ. Health Rep. 2018, 5, 375–386.
49. Dehaut, A.; Cassone, A.-L.; Frère, L.; Hermabessiere, L.; Himber, C.; Rinnert, E.; Rivière, G.; Lambert, C.; Soudant, P.; Huvet, A.; et al. Microplastics in seafood: Benchmark protocol for their extraction and characterization. Environ. Pollut. 2016, 215, 223–233.
50. Ellen MacArthur Foundation. The New Plastics Economy: Rethinking the Future of Plastics; Ellen MacArthur Found: Cowes, UK, 2016; p. 120.

51. European Commission. A Sustainable Bioeconomy for Europe: Strengthening the Connection between Economy, Society and the Environment; European Commission: Brussels, Belgium, 2018; ISBN 9789279941450.

52. European Commission. A European Strategy for Plastics in a Circular Economy; European Commission: Brussels, Belgium, 2018.

53. Sander, M.; Filatova, T.; Weber, M. Biodegradability of Plastics in the Open Environment; ETH Zurich: Zürich, Switzerland, 2020; ISBN 9783982030180.

54. European Commission Directorate-General for Environment. Plastic Waste in the Environment—Final Report; European Commission: Brussels, Belgium, 2011; p. 171.

55. Garlotta, D. A Literature Review of Poly(Lactic Acid). J. Polym. Environ. 2001, 9, 63–84.

56. Madhavan Nampoothiri, K.; Nair, N.R.; John, R.P. An overview of the recent developments in polylactide (PLA) research. Bioresour. Technol. 2010, 101, 8493–8501.

57. Chanprateep, S. Current trends in biodegradable polyhydroxyalkanoates. J. Biosci. Bioeng. 2010, 110, 621–632.

58. Xu, J.; Guo, B.H. Poly(butylene succinate) and its copolymers: Research, development and industrialization. Biotechnol. J. 2010, 5, 1149–1163.

59. Siracusa, V.; Blanco, I. Bio-Polyethylene (Bio-PE), Bio-Polypropylene (Bio-PP) and Bio-Poly(ethylene terephthalate) (Bio-PET): Recent Developments in Bio-Based Polymers Analogous to Petroleum-Derived Ones for Packaging and Engineering Applications. Polymers 2020, 12, 1641.

60. Labet, M.; Thielemans, W. Synthesis of polycaprolactone: A review. Chem. Soc. Rev. 2009, 38, 3484.

61. Aslam, M.; Kalyar, M.A.; Raza, Z.A. Polyvinyl alcohol: A review of research status and use of polyvinyl alcohol based nanocomposites. Polym. Eng. Sci. 2018, 58, 2119–2132.

62. Ferreira, F.V.; Cividanes, L.S.; Gouveia, R.F.; Lona, L.M.F. An overview on properties and applications of poly(butylene adipate- co -terephthalate)-PBAT based composites. Polym. Eng. Sci. 2019, 59, E7–E15.

63. Auras, R.; Lim, L.-T.; Selke, S.E.M.; Tsuji, H. (Eds.) Poly(Lactic Acid); John Wiley & Sons, Inc.: Hoboken, NJ, USA, 2010; Volume 53, ISBN 9780470649848.

64. Drumright, R.E.; Gruber, P.R.; Henton, D.E. Polylactic Acid Technology. Adv. Mater. 2000, 12, 1841–1846.

65. Mehta, R.; Kumar, V.; Bhunia, H.; Upadhyay, S.N. Synthesis of poly(lactic acid): A review. J. Macromol. Sci. Polym. Rev. 2005, 45, 325–349.

66. Pantani, R.; Sorrentino, A. Influence of crystallinity on the biodegradation rate of injection-moulded poly(lactic acid) samples in controlled composting conditions. Polym. Degrad. Stab. 2013, 98, 1089–1096.
67. Perego, G.; Cella, G.D.; Bastioli, C. Effect of molecular weight and crystallinity on poly(lactic acid) mechanical properties. J. Appl. Polym. Sci. 1996, 59, 37–43.
68. Auras, R.; Harte, B.; Selke, S. An Overview of Polylactides as Packaging Materials. Macromol. Biosci. 2004, 4, 835–864.
69. Castro-Aguirre, E.; Iñiguez-Franco, F.; Samsudin, H.; Fang, X.; Auras, R. Poly(lactic acid)—Mass production, processing, industrial applications, and end of life. Adv. Drug Deliv. Rev. 2016, 107, 333–366.
70. Cicala, G.; Giordano, D.; Tosto, C.; Filippone, G.; Recca, A.; Blanco, I. Polylactide (PLA) Filaments a Biobased Solution for Additive Manufacturing: Correlating Rheology and Thermomechanical Properties with Printing Quality. Materials 2018, 11, 1191.
71. Meraldo, A. Introduction to Bio-Based Polymers; Elsevier Inc.: Amsterdam, The Netherlands, 2016; ISBN 9780323371001.
72. Bechthold, I.; Bretz, K.; Kabasci, S.; Kopitzky, R.; Springer, A. Succinic acid: A new platform chemical for biobased polymers from renewable resources. Chem. Eng. Technol. 2008, 31, 647–654.
73. Gigli, M.; Fabbri, M.; Lotti, N.; Gamberini, R.; Rimini, B.; Munari, A. Poly(butylene succinate)-based polyesters for biomedical applications: A review. Eur. Polym. J. 2016, 75, 431–460.
74. Aditiya, H.B.; Mahlia, T.M.I.; Chong, W.T.; Nur, H.; Sebayang, A.H. Second generation bioethanol production: A critical review. Renew. Sustain. Energy Rev. 2016, 66, 631–653.
75. Vroman, I.; Tighzert, L. Biodegradable polymers. Materials 2009, 2, 307–344.
76. Law, R.C. 5. Applications of cellulose acetate 5.1 Cellulose acetate in textile application. Macromol. Symp. 2004, 208, 255–266.
77. Rustemeyer, P. 5.2 CA filter tow for cigarette filters. Macromol. Symp. 2004, 208, 267–292.
78. Shibata, T. 5.6 Cellulose acetate in separation technology. Macromol. Symp. 2004, 208, 353–370.
79. Fischer, S.; Thümmler, K.; Volkert, B.; Hettrich, K.; Schmidt, I.; Fischer, K. Properties and applications of cellulose acetate. Macromol. Symp. 2008, 262, 89–96.
80. Puls, J.; Wilson, S.A.; Hölter, D. Degradation of Cellulose Acetate-Based Materials: A Review. J. Polym. Environ. 2011, 19, 152–165.
81. Rose, M.; Palkovits, R. Cellulose-Based Sustainable Polymers: State of the Art and Future Trends. Macromol. Rapid Commun. 2011, 32, 1299–1311.

82. Wang, S.; Lu, A.; Zhang, L. Recent advances in regenerated cellulose materials. Prog. Polym. Sci. 2016, 53, 169–206.
83. Chen, J. Synthetic Textile Fibers. In Textiles and Fashion; Elsevier: Amsterdam, The Netherlands, 2015; pp. 79–95.
84. Liu, H.; Xie, F.; Yu, L.; Chen, L.; Li, L. Thermal processing of starch-based polymers. Prog. Polym. Sci. 2009, 34, 1348–1368.
85. Zhang, Y.; Rempel, C.; Liu, Q. Thermoplastic Starch Processing and Characteristics—A Review. Crit. Rev. Food Sci. Nutr. 2014, 54, 1353–1370.
86. Da Róz, A.L.; Carvalho, A.J.F.; Gandini, A.; Curvelo, A.A.S. The effect of plasticizers on thermoplastic starch compositions obtained by melt processing. Carbohydr. Polym. 2006, 63, 417–424.
87. Lörcks, J. Properties and applications of compostable starch-based plastic material. Polym. Degrad. Stab. 1998, 59, 245–249.
88. Santana, Á.L.; Angela, A.; Meireles, M. New Starches are the Trend for Industry Applications: A Review. Food Public Health 2014, 4, 229–241.
89. Mohamad Yazid, N.S.; Abdullah, N.; Muhammad, N.; Matias-Peralta, H.M. Application of Starch and Starch-Based Products in Food Industry. J. Sci. Technol. 2018, 10.
90. Samsudin, H.; Hani, N.M. Use of Starch in Food Packaging. In Starch-Based Materials in Food Packaging; Elsevier: Amsterdam, The Netherlands, 2017; pp. 229–256.
91. Rehm, B.H.A. Bacterial polymers: Biosynthesis, modifications and applications. Nat. Rev. Microbiol. 2010, 8, 578–592.
92. Wang, Y.; Yin, J.; Chen, G.-Q. Polyhydroxyalkanoates, challenges and opportunities. Curr. Opin. Biotechnol. 2014, 30, 59–65.
93. Lee, S.Y. Bacterial polyhydroxyalkanoates. Biotechnol. Bioeng. 2000, 49, 1–14.
94. Reddy, C.S.K.; Ghai, R.; Kalia, V. Polyhydroxyalkanoates: An overview. Bioresour. Technol. 2003, 87, 137–146.
95. Kathiraser, Y.; Aroua, M.K.; Ramachandran, K.B.; Tan, I.K.P. Chemical characterization of medium-chain-length polyhydroxyalkanoates (PHAs) recovered by enzymatic treatment and ultrafiltration. J. Chem. Technol. Biotechnol. 2007, 82, 847–855.
96. Keshavarz, T.; Roy, I. Polyhydroxyalkanoates: Bioplastics with a green agenda. Curr. Opin. Microbiol. 2010, 13, 321–326.
97. Hazer, B.; Steinbüchel, A. Increased diversification of polyhydroxyalkanoates by modification reactions for industrial and medical applications. Appl. Microbiol. Biotechnol. 2007, 74, 1–12.

98. Chen, G.; Wang, Y. Medical applications of biopolyesters polyhydroxyalkanoates. Chin. J. Polym. Sci. 2013, 31, 719–736.
99. ISO Online Browsing Platform. Available online: (accessed on 1 November 2020).
100. CEN Online Standards Search. Available online: (accessed on 1 November 2020).
101. Folino, A.; Karageorgiou, A.; Calabrò, P.S.; Komilis, D. Biodegradation of wasted bioplastics in natural and industrial environments: A review. Sustainability 2020, 12, 6030.
102. Briassoulis, D.; Degli Innocenti, F. Standards for Soil Biodegradable Plastics. In Soil Degradable Bioplastics for a Sustainable Modern Agriculture; Springer: Berlin/Heidelberg, Germany, 2017; pp. 139–168.
103. Emadian, S.M.; Onay, T.T.; Demirel, B. Biodegradation of bioplastics in natural environments. Waste Manag. 2017, 59, 526–536.
104. Ahn, H.K.; Huda, M.S.; Smith, M.C.; Mulbry, W.; Schmidt, W.F.; Reeves, J.B. Biodegradability of injection molded bioplastic pots containing polylactic acid and poultry feather fiber. Bioresour. Technol. 2011, 102, 4930–4933.
105. Tabasi, R.Y.; Ajji, A. Selective degradation of biodegradable blends in simulated laboratory composting. Polym. Degrad. Stab. 2015, 120, 435–442.
106. Lucas, N.; Bienaime, C.; Belloy, C.; Queneudec, M.; Silvestre, F.; Nava-Saucedo, J.E. Polymer biodegradation: Mechanisms and estimation techniques—A review. Chemosphere 2008, 73, 429–442.
107. Haider, T.P.; Völker, C.; Kramm, J.; Landfester, K.; Wurm, F.R. Plastics of the Future? The Impact of Biodegradable Polymers on the Environment and on Society. Angew. Chem. Int. Ed. 2019, 58, 50–62.
108. Fojt, J.; David, J.; Přikryl, R.; Řezáčová, V.; Kučerík, J. A critical review of the overlooked challenge of determining micro-bioplastics in soil. Sci. Total Environ. 2020, 745, 140975.
109. Flemming, H.C. Relevance of biofilms for the biodeterioration of surfaces of polymeric materials. Polym. Degrad. Stab. 1998, 59, 309–315.
110. Gu, J.D. Microbiological deterioration and degradation of synthetic polymeric materials: Recent research advances. Int. Biodeterior. Biodegrad. 2003, 52, 69–91.
111. Pauli, N.-C.; Petermann, J.S.; Lott, C.; Weber, M. Macrofouling communities and the degradation of plastic bags in the sea: An in situ experiment. R. Soc. Open Sci. 2017, 4, 170549.