Formulating Bioplastic Composites for Biodegradability, Recycling, and Performance: A Review

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Society's wish list for future packaging systems is placing some daunting challenges upon researchers: In addition to protecting contents during storage and shipping, the material must not bio-accumulate, and it should be readily recyclable by using practical processing steps. This article considers strategies employing bio-based plastics and reviews published information relative to their performance. Though bioplastics such as poly(lactic acid) (PLA) and poly(hydroxybutyrate) (PHB) can be prepared from plant materials, their default properties are generally inferior to those of popular synthetic plastics. In addition, some bioplastics are not easily decomposed in soil or seawater, and the polymers can undergo chemical breakdown during recycling. This review considers strategies to overcome such challenges, including the use of biodegradable cellulose-based reinforcing particles. In addition to contributing to strength, the cellulose can swell the bioplastic, allowing enzymatic attack. The rate-controlling step in bioplastic degradation also can be abiotic, *i.e.* not involving enzymes. Though there is much more work to be done, much progress has been achieved in formulating bioplastic composites that are biodegradable, recyclable, and higher in strength compared to the neat polymer. Emphasis in this review is placed on PLA and PHB, but not to the exclusion of other bioplastic matrix materials.

Keywords: Poly(lactic acid); Poly(hydroxybutyrate); Cellulosic reinforcement; Decomposition; Engineered biodegradation; Lipase; Cellulase

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INTRODUCTION

Plastic materials are playing an ever-increasing role in modern society. A plastic can be defined as a polymeric material that can be formed by flow, which often involves cycles of melting and then cooling in order to optimize the final product qualities. The most widely used plastics are petroleum-derived synthetic polymers, which are meltable and hydrophobic. They include polyethylene, polypropylene, polyamides, and polyesters. Environmental damage occurs when such plastics are discarded as litter after a single use (*e.g.*, as food packaging). The non-biodegradable nature of typical synthetic plastics means that they tend to accumulate in ecosystems, including in the ocean, where they interfere with aquatic life (Cózar *et al.* 2014; Eriksen *et al.* 2014; Jambeck *et al.* 2015; The Pew Charitable Trust 2020).

This article reviews studies that explore potential ways to replace petroleum-based plastics with bio-based plastics. Emphasis here is on hard plastics that can be used for such items as bottles, cups, and components of various devices. Efforts to replace petroleum-based plastics in such applications face three serious challenges: first, bio-based systems will need to be biodegradable under typical conditions prevailing not only in soils, but also in the sea; second, public pressure will demand them to be recyclable multiple times, which may be achievable by melting and compounding, and third, the bio-based systems will need to meet rigorous performance standards related to strength, toughness, and resistance to fluids, *etc.* Costs of bio-plastics are a concern, since market forces are likely to be a major factor governing the potential volume of implementation.

Of the challenges just mentioned, the goal of full, undisputed biodegradability is perhaps the most daunting. Biodegradability will be defined here as the ability of a material to be broken down by living organisms into simple molecules such as water, carbon dioxide, methane, and other compounds that can be utilized by living organisms. Leja and Lewandowicz (2010), further defined biodegradation as involving the metabolism of microorganisms such as bacteria, fungi, and algae. According to ISO Standard 14855-1:2005, a biodegradable plastic is one that attains 90% mineralization of organic carbon when exposed to defined conditions. By contrast, thermal decomposition is an example of a breakdown mechanism of bioplastic that does not depend on microorganisms or the enzymes produced by them (Petinakis *et al.* 2010). As noted by Shen *et al.* (2009) and Lavoine and Bras (2016), there is a societal preference for packaging materials that are both biodegradable and derived from plant materials, *i.e.* bio-based.

The term biodegradability encompasses a wide variety of enzymatic and/or chemical processes induced by living organisms, whose efficiencies are influenced to a great degree by the state of the local environment of the living organism. For example, rates for biodegradation can vary widely because of water and soil conditions. These rates are therefore not a constant for a particular substrate. Furthermore, the path of biodegradation is dependent on oxygen, leading to aerobic or anaerobic processes (Jørgensen 2008). A series of biodegradation studies have been completed that collected data on the nature of the biodegradation for the most common synthetic plastics (Table 1). It should be noted that for each of the studies, there were numerous sources and types of plastics that greatly influenced the overall incubation times, weight losses, and degradation products. For example, Shah *et al.* (2008), found that the rate of biodegradation of polyurethane (PUR) under the same conditions as those by Stepien *et al.* (2017) could be significantly reduced to 28 days when using a cocktail of bacteria (*Bacillus* sp. AF8; *Pseudomonas* sp. AF9; *Micrococcus* sp. 10; *Arthrobacter* sp. AF11; *Corynebacterium* sp.

AF12). Through a natural evolutionary process, microorganisms can adapt their cocktail of enzymes to enable the biodegradation of diverse food sources, including plastics. For instance, researchers discovered a natural enzyme in a Japanese waste recycling center; the bacterium was able to efficiently degrade poly(ethyleneterephthalate) (PET) as a food source (Austin *et al*. 2018).

Table 1. Biodegradation of Synthetic Plastics under Specified Conditions and Microorganism

Type of Plastic	Micro-organism(s)	Isolated Source	Incubation Time, d	Weight Loss, %	Degradation Products	References
PE (LDPE film)	*Rhodococcus ruber* C208	Disposal site	30	4	ND	Orr *et al.* 2004
PS (film)	*Rhodococcus ruber* C208	Disposal site	56	0.8	ND	Mor & Sivan 2008
PP (film & pellets)	*Aneurinibacillus aneurinilyticus*; *Brevibacillus agri*; *Brevibacillus* sp.; *Brevibacillus brevis*	Landfills and sewage	140	22.8-27.0	Detected	Skariyachan *et al.* 2018
PVC (plasticized)	*Pseudomonas citronellolis*	Soil	45	13	ND	Giacomucci *et al.* 2019
PUR (Polyether PUR film)	*Pseudomonas denitrificans*, *Pseudomonas fluorescens*, *Bacillus subtilis*, *Yarrowia lipolytica*	Soil	150	2.8-10.5	ND	Stepien *et al.* 2017

Key: PE = polyethylene; LDPE = low-density polyethylene; PS = polystyrene; PP = polypropylene; PVC = poly(vinylchloride); PUR = poly(urethane)

Table 2. Biodegradation of Bioplastics under Specified Conditions

Plastic Type	Conditions	Isolated Source	Incubation Time, d	Weight Loss, %	Degradation Products	References
PLA (powder)	25 °C, 60% humidity	Soil	28	13.8	NA	Adhikari *et al.* 2016
PHA (film)	35% moisture	Soil	60	35	NA	Wu 2014
PHB (molded container)	aerobic	Soil	18	18	NA	Woolnough *et al.* 2008
Starch (jar)	20 °C, 60% moisture	Soil	110	14.2	CO_2	Gómez & Michel 2013
Cellulose (sponge cloth)	Aerobic, 58 °C	Soil	154	> 80	ND	Vaverková *et al.* 2015

Key: PLA = poly(lactic acid); PHA = poly(hydroxyalkanoate); PHB = poly(hydroxybutyrate)

Research on bioplastic biodegradation also has been conducted, and some results are listed in Table 2. What is noteworthy to observe between the bioplastics versus the synthetic plastics is that the incubation periods were similar, while resultant weight losses were only a little bit higher for bioplastics.

The fact that a certain polymer has been prepared from plant-based source materials does not imply that it is readily biodegradable (Payne *et al.* 2019). Rather, there appears to be a perverse inverse relationship between the ability of polymers to achieve high elastic modulus and melting point *vs.* their susceptibility to degradation at ambient temperature (Bikiaris 2013; Elsawy *et al.* 2017). A prime example is poly(lactic acid) (PLA), which has received attention as a leading candidate to substitute for synthetic polymers in applications requiring stiffness (Farah *et al.* 2016). Though some studies support the biodegradability of PLA under ideal composting conditions at relatively high temperatures (Kale *et al.* 2007a; Rudnick and Birassoulis 2011; Siracusa 2019), unmodified PLA generally cannot be regarded as biodegradable at room temperature or in typical ocean conditions (Emadian *et al.* 2017; Chamas *et al.* 2020). On the other hand, studies have shown that the properties of various plastics can be improved by judicious use of cellulose-based reinforcements, especially if something is done to improve the compatibility between the surfaces of the reinforcing particles and various hydrophobic matrix polymers (Hubbe and Grigsby 2020).

As will be shown in this review article, progress in achieving each of the three main goals – biodegradability, recyclability, and performance – already has been demonstrated. Such success often has been achieved by the use of reinforcing particles and various additives. Each modification adds to the complexity of the formulation. Formulation of a complex composite structure, especially if it needs to contain multiple additives to optimize multiple aspects of its performance, can make it more difficult to adjust the process to meet quality requirements. Thus, as has been found in other fields, complexity itself can be regarded as an additional challenge faced by innovators (Place *et al.* 2009; Geraldi *et al.* 2011).

Working Hypotheses

The premise of this review article is that the three goals of biodegradability, recyclability, and performance might be best met, or at least approached, by formulation of a composite system having a blend of ingredients. The biodegradability can be measured by published assays and standards (which are specified later in the article). The word recyclability, for the present discussion, will mean that the material can be melt-reprocessed and formed into successive generations of plastic material that can serve a similar function as in the first cycle. The word "performance" will be considered relative to common petroleum-based plastics such as polyethylene, polypropylene, and polystyrene, which constitute a substantial portion of non-biodegradable litter.

The following hypotheses are proposed here as a means of focusing attention on certain issues that will be considered in this article. Published evidence supporting or not supporting the hypotheses listed below will be considered in this article.

1. Fiber-like or fibrillated cellulosic reinforcements have the potential not only to strengthen bioplastic matrix materials, but they also can provide a conduit to allow moisture and enzymes, *etc.*, to gain access within the structure, promoting the possibility of biodegradation.

2. The manner in which the surfaces of cellulosic reinforcements are treated or derivatized can provide not only an enhancement of blend compatibility and strength properties, but it also can provide a strategic weak link by which the structure may be later degraded by natural microbes and/or enzymes.
3. The physical properties of the composite, as well as its recyclability and/or biodegradability, can be optimized by the selection and concentration of additives such as plasticizers, surfactants, and other bio-based polymers such as starch and its derivatives.
4. The biodegradation of crystalline domains of a bioplastic matrix polymer such as PLA can be enhanced by including ingredients that contain carboxylic acid groups. Such materials may need to become intimately mixed during casting or compounding of the material.

The hypothesis statements listed above all deal with aspects of sustainability. A sustainable material ought to fulfil a useful purpose with a minimum of adverse impact on the environment. Polymeric products based on the use of plant-based materials and eco-friendly processing have the potential to reduce society's dependence on fossil fuels (Kobayashi 2017). The importance of direct recycling of plastics is highlighted by the work of Souroudi and Jakubowicz (2013) and Cosate de Andrade *et al.* (2016). Their life cycle assessment studies showed that in the case of PLA, simple recycling of the used plastic, by means of melting and reforming into new products, had a lower adverse environmental impact than either chemical recycling (for instance to obtain lactic acid) or composting. Composting is often discussed as a suitable end-of-life fate for bioplastics, since by that means their organic content theoretically can contribute to amendment of soils (Payne *et al.* 2019). However, composting is only adoptable if the "recoverable" materials are susceptible to biological attack without compromising the composting ecosystem in which they are present. A compostable material offers a digestible substrate that does not kill the microorganisms directly or indirectly by virtue of its by-products. A life cycle study by Hermann *et al.* (2011) concluded that favorable results in terms of energy recovery could be achieved if a bioplastic is anaerobically degraded with recovery of methane gas, which can displace the use of fossil fuels. Regardless of what is planned for the end fate of a new generation of bioplastic materials, given the huge amounts of plastics that are ending up in natural waters and soils around the world, they must be biodegradable under the conditions that they are likely to encounter in outdoor and aquatic environments.

Layout of the Article

The main sections of this article are reflective of the three societal expectations for bioplastics, as mentioned earlier. However, to make that discussion more understandable for a wide audience, some critical background information is presented in the next main selection. After that comes a section discussing factors that have been reported to affect the rates of biodegradation of bioplastics and their composites or blends. The next main section has to do with the recycling of bioplastics, with emphasis on recycling of the plastic material into new generations of plastic material. Then the attention is turned to how to improve the strength and other physical attributes of bioplastics and their composites.

Earlier Reviews

Because of widespread concern about the fate and properties of plastics, including bioplastics, many review articles and chapters have been written that illuminate aspects of the topic. Selected works of this type are listed in Table 3. The present article focuses on opportunities to apply a variety of strategies to optimize not only the biodegradation, but also recyclability and strength-related properties.

Table 3. Review Articles and Chapters Dealing with Aspects of Bioplastics

Topic	**Reference**
Nanocomposites of aliphatic polyesters, such as PLA	Bikiaris 2013
PLA mass production, processing, applications, end-of-life	Castro-Aguirre *et al.* 2016
Biotechnology advances for lactic acid production	Cubas-Cano *et al.* 2018
Biodegradable plastics for food packaging	Din *et al.* 2020
Biodegradation of bioplastics in natural environments	Emadian *et al.* 2017
PLA physical and mechanical properties relative to applications	Farah *et al.* 2016
Cellulose fiber-reinforced PLA composites and applications	Graupner *et al.* 2009
Cellulose-based nanocomposites	Hubbe *et al.* 2008
Particle size *vs.* strength of cellulose-reinforced plastic composites	Hubbe & Grigsby 2020
Biodegradable polyesters for medical and other applications	Ikada & Tsuji 2000
Compostability of bioplastic packaging materials	Kale *et al.* 2007b
Green polymer synthesis based on renewable materials	Kobayashi 2017
Polymer biodegradation mechanisms and assessment	Lucas *et al.* 2008
Biobased plastics, including effects of plasticizers	Mekonnen *et al.* 2013
Biodegradable fibers, polymers, and composites	Mohanty *et al.* 2000
PLA-based biopolymers reinforced by natural fibers	Mukherjee & Kao 2011
PLA composites, with an emphasis on drug delivery	Murariu & Dubois 2016
Bio-based and degradable plastics	Narayan 2012
Patents related to the recycling of biopolymers	Niaounakis 2019
Biodegradable nanocomposites, including polyhydroxyalkanoates	Pandey *et al.* 2005
Biodegradation of PLA with emphasis on enzymes	Qi *et al.* 2017
Blending of poly(hydroxybutyrate) with other polymers	Quental *et al.* 2010
Polyhydroxyalkanoates, including their biodegradability	Reddy *et al.* 2003
Polyhydroxybutyrate and its enzymatic degradation	Roohi *et al.* 2018
Wood-thermoplastic composites	Rowell 2007
Methods to quantify biodegradation of bioplastics	Ruggero *et al.* 2019
Biodegradation of films of biobased polymers	Scaffaro *et al.* 2019
Plastics biodegradation in soils as an end-of-life option	Scalenghe 2018
Biodegradation of synthetic biopolymers	Siracusa 2019
Recycling of bioplastics, emphasizing mechanical recycling	Soroudi & Jakubowicz 2013
Use of nanoparticles as reinforcement in bioplastics	Souza & Fernando 2016
PLA biodegradation, with focus in microbes and enzymes	Tokiwa & Calabia 2006
Polyester biodegradation, with focus in microbes and enzymes	Tokiwa & Calabia 2007
Polymer biodegradation, with focus in microbes and enzymes	Tokiwa *et al.* 2009
Microbial enzymes involved in degradation of bioplastics	Urbanek *et al.* 2020
Biodegrading PLA, polycaprolactone, & poly(propylene carbonate)	Xu *et al.* 2020
Blends of cellulose nanocrystals with natural & synthetic polymers	Younas *et al.* 2019
Polyglycerol hyperbranched polyesters and their applications	Zamboulis *et al.* 2019

CRITICAL BACKGROUND INFORMATION

Bioplastics as a Potential Path Forward

Certain bioplastics, when used alone, already have advanced a lot towards meeting society's needs for biodegradability, recyclability, and strength. According to Emadian *et al.* (2017), bioplastics in general tend to be more expensive and lower in strength than their petroleum-based alternatives. Their redeeming feature is that they are predominantly polyesters. Ester bonds, in general, are expected to be susceptible to cleavage by enzymatic action. Esterases have evolved to convert polyesters to monomeric compounds. Their catalytic power can be quantified in terms of their catalytic acceleration k_{cat}/k_u, where k_u is the rate constant of a nonenzymatic ester hydrolysis. For example, the value of catalytic acceleration for acetylchoinersterase, the enzyme necessary for support proper neuronal communication pathways, is 10^{13} (Harel *et al.* 1996). Such values are consistent with a high level of molecular recognition playing an essential role in the hydrolytic process.

Din *et al.* (2020) provide a quite comprehensive review of the most widely available bioplastics, *i.e.* poly(lactic acid) (PLA), polyhydroxyalkanoates, including poly(hydroxyl-butyrate) (PHB), polycaprolactone, thermoplasticized starch, and cellulose. Emadian *et al.* (2017) tabulate many studies in which the extents of biodegradation were reported as a function of conditions and time of contact with soil, composting, or exposure floating on the sea. Panchal and Vasava (2020) emphasized that there is an essentially infinite range of variants of biodegradable polymer materials that can be achieved by making adjustments of composition and conditions during synthetic steps. Thus, even if the presently available biopolymers and their blends or composites do not yet meet all of the hoped-for goals, there is reason to be hopeful that better formulations will continue to emerge during the course of research.

Chemistries of Bioplastics

PLA basics

The first type of bioplastic to be considered here will be PLA. Lactic acid, from which PLA is ultimately derived, can be generated as a byproduct of polysaccharides or sugars. The polymerization can take place under water-free conditions to yield a polymer having the repeat unit shown in Fig. 1. The most promising synthetic route involves dimerization into lactide with the loss of two water molecules, followed by polymerization in anhydrous media in the presence of tin octanoate as a catalyst (Omay and Guvenilir 2013; Castro-Aguirre *et al.* 2016). As shown, PLA is a linear polyester. Because the repeating unit lacks any charged groups or –OH groups, PLA can be regarded as hydrophobic, though less so than polyolefins such as polyethylene, polypropylene, or poly(ethylene terephthalate (PET). Especially when PLA is prepared with relatively high molecular weight and pure stereochemistry (Reeve *et al.* 1994), a melting point as high as 175 °C can be achieved, which is exceptionally high among biopolymers (Bikiaris 2013). Under favorable conditions, superior optical and physical properties can be achieved (Miyoshi *et al.* 1996). Potentially disadvantageous traits of PLA can be listed as its brittle nature, low resistance to heat, and a slow rate of crystallization, the last of which means that PLA tends to fall short of its potential elastic modulus values (Elsawy *et al.* 2017). The limited tolerance for heating can lead to loss of molecular weight during melt-preprocessing (Farah *et al.* 2016). Though PLA can be regarded as not very compatible with cellulosic surfaces, it is not the worst case. The development of contact with cellulosic reinforcements with PLA is better than that between cellulosic surfaces and polyethylene or polypropylene (Mofokeng *et al.* 2012; Hubbe and Grigsby 2020).

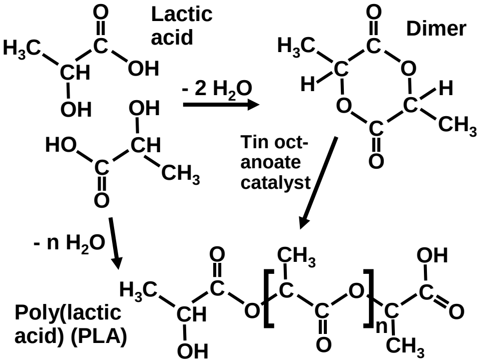

Fig. 1. Main synthesis routes and structure of poly(lactic acid)

Another limitation of PLA, which will be covered in the next main section, is the lack of, or very slow rate of biodegradation at ambient temperatures (Karamanlioglu and Robson 2013; da Silva *et al.* 2019). Slow biodegradation, especially of the crystalline zones of PLA, appears to be the flip side of successful preparation of a dense, well-organized nanostructure. Although this is a bonus for its use in mechanically demanding applications, the presence of crystalline zones makes PLA more recalcitrant against biodegradation. In addition, the hydrophobic nature of PLA discourages the diffusion of water, ions, or enzymes into the interior of PLA.

Because optically pure PLA, *e.g.* poly(*L*-lactic acid), generally can develop higher crystallinity, melting point, and modulus values, it can be advantageous to use a fermentation route to obtain the starting lactic acid of high L-enantiomer purity (Abdel-Rahman *et al.* (2013). Singhvi and Gokhale (2013) have reviewed aspects of production of PLA from biomass. Cubas-Cano *et al.* (2018) reviewed the microbial aspects of lactic acid production, with emphasis on metabolic pathways and purification steps. In addition, as shown by Chambon *et al.* (2011), lactic acid can be obtained by hydrothermal degradation of cellulose.

PHB and other polyalkanoates

When the overarching goal is to find a biopolymer that can serve as a substitute for common petroleum-based polymers, the next most often considered option, after PLA, appears to be poly(3-hydroxybutyrate) (PHB), along with its copolymer with valeric acid (PHB-co-valerate) (Reddy *et al.* 2003). Unmodified PHB has been reported to be quite brittle, making it difficult to reprocess during melting and reforming (Soroudi and Jakubowicz 2013; Seggiani *et al.* 2015). PHB is derived when bacteria are allowed to thrive in a glucose-controlled environment and later experience nutrient deprivation, leading to carbon assimilation in the course of PHB production. This biomaterial and associated manufacturing expenditures deliver a much smaller ecological footprint than the petroleum analogues.

The copolymer of PHB with valeric acid has more favorable processing ability and is more suitable for simple recycling (Ariffin *et al.* 2010; Soroudi and Jakubowicz 2013; Lagazzo *et al.* 2019). Valeric acid ($CH_3(CH_2)_3COOH$), which is also known as pentanoic acid, is a straight-chain low MW carboxylic acid that can be easily degraded. Favorable adhesion to cellulosic fibers with PHB-co-valerate was reported in a study of melt-compounding (Sanchez-Safont *et al.* 2016). Lagazzo *et al.* (2019) showed that composites formed with the copolymer and sisal fibers could be successfully melt-reprocessed three times, and there was less embrittlement compared to the unreinforced copolymer. Losses in molecular mass have been reported, in the course of melt-reprocessing; however, such losses did not prevent multiple recycling of the copolymer (Zaverl *et al.* 2012; Vandi *et al.* 2019). Yu *et al.* (2011, 2014a) and Srithep *et al.* (2013) reported that composites formed from PHB-co-valerate and nanofibrillated cellulose (NFC) showed earlier onset of crystallinity of the matrix phase, which contributed to more favorable physical properties. Relative to PLA, PHB-co-valerate has been reported to have a faster rate of biodegradation in sludge and in soil (Avella *et al.* 2000; Arcos-Hernandez *et al.* 2012). Soil biodegradation of PHB-co-valerate was favorably affected by the presence of wood fibers (up to 50 wt%), as a composite (Chan *et al.* 2019). The same study evaluated wood-PLA composites, and the biodegradation results were not as promising as for PHB-co-valerate. Weng *et al.* (2011) reported more rapid biodegradation of PHB that had been blended with either PHB-co-valerate or isomeric forms of PHB.

The copolymer also can be hydrolytically degraded, though not as favorably as in the case of PLA (Bonartsev *et al.* 2012a,b). Hassaini *et al.* (2017) observed improved physical properties of PHB-co-valerate composites formed with olive husk flour that had been hydrophobized with trimethoxy-octadecylsilane to render the reinforcing fibers more hydrophobic. Yatigala *et al.* (2018) similarly showed that addition of maleic anhydride during compounding improved the properties of several kinds of bioplastics, including PHB-co-valerate, with wood fiber reinforcement.

As shown in Fig. 2, PHB can be obtained in different isomeric forms, depending on the starting material and the synthesis route (Sastri 2010).

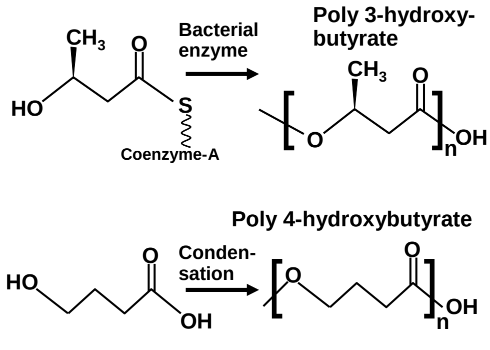

Fig. 2. Synthesis reactions and structures of two isomeric forms of poly(hydroxybutyrate)

Starch products

Starch products deserve to be mentioned here because they have potential for blending with hydrophobic bioplastics such as PLA. In that way, starch can play a role in formulations that substitute for commercial, petroleum-derived plastics. In the presence of optimized moisture content and temperature, it is possible to extrude starch as a thermoplastic polymer (Kalambur and Rizvi 2006; Elsawy *et al.* 2017; Khan *et al.* 2017; Din *et al.* 2020). Blends of PLA and thermoplasticized starch have been widely studied (Martin and Averous 2001; Ganjyal *et al.* 2007; Thongtan and Sriroth 2011; Nair *et al.* 2012; Mihai *et al.* 2014; Masmoudi *et al.* 2016; Lv *et al.* 2017; de Macedo *et al.* 2019;

Turco *et al.* 2019). An especially attractive feature of starch, as a candidate for blending with other biopolymers, is its generally rapid biodegradation by amylase enzymes (Ganjyal *et al.* 2007; Tokiwa and Calabia 2007; Lu *et al.* 2009; Leejarkpai *et al.* 2011; Narayan 2012; Lv *et al.* 2017; Sohn *et al.* 2019; Ferreira *et al.* 2020).

Researchers have wondered why it has been possible, given the generally hydrophilic and water-soluble nature of starch, to achieve effective blends with biopolymers such as PLA. Lawton (1995) reported a surface energy of extruded and jet-cooked starch films of about 40 dynes/cm, which is moderately hydrophilic. Averous and Fringant (2001) found that addition of 10% polyester in a blend with starch yielded a much more hydrophobic surface, which is consistent with a disproportionate amount of the more hydrophobic component diffusing to the air interface. Biresaw and Carrier (2001) did not find any consistent correlation between the ability of starch to be blended with various polymers and the wettability properties of the other polymers. More recently, Shrimali *et al.* (2018) presented evidence that a hydrophobic side of starch macromolecules is able to adsorb effectively onto hydrophobic mineral surfaces. In other words, depending on the conformation of starch, it can present a surface that is suitably hydrophobic to be compatible with a hydrophobic plastic phase. The effect was explained by Yamane *et al.* (2006), who considered analogous behavior of cellulose, which has the same chemical composition as amylose starch, but with different orientation at the glycosidic linkages. As shown in Fig. 3, depending on whether one is dealing with the axial or the equatorial face of cellulose, it can be alternatively hydrophobic or hydrophilic (Khazraji and Sylvain (2013). Thus, it would be reasonable to expect that a related mechanism can be important when thermoplasticized starch is being formulated in mixtures with more hydrophobic bioplastics.

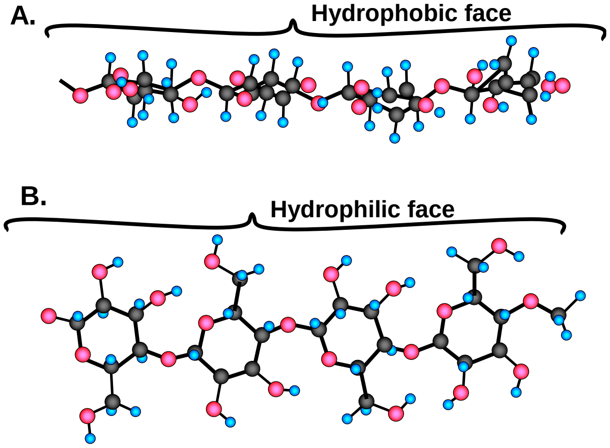

Fig. 3. Molecular conformation of cellulose, redrawn from Yamane *et al.* (2006), who used the drawing to support their finding that cellulose can present surfaces of differing hydrophobic or hydrophilic character, depending on the solvent system present during regeneration of the polymer. In the figure, gray spheres represent carbon, pink spheres represent oxygen, and cyan spheres represent hydrogen.

A further example to highlight the dual affinity of starch is provided by cyclic forms of starch, which are known as cyclodextrins. Through the action of specialized enzymes, starch can be cyclized into various ring structures comprising 5 to 7 anhydroglucose units; these are known respectively as α, β, and δ (Roy *et al.* 2015). Figure 4 shows the molecular structure of a β-cyclodextrin version (part A) and the conformational pattern of a δ-cyclodextrin version in which the hydrophobic nature is stereochemically amplified (part B). In the toroidal structure, the hydroxyl groups face outwards toward the bulk solution, hence imbuing the outer part of the ring with hydrophilicity (dissolves well in water). By contrast, the hydrophobic components (C-H bond) nest within the cavity of the toroid to endow that location with hydrophobicity.

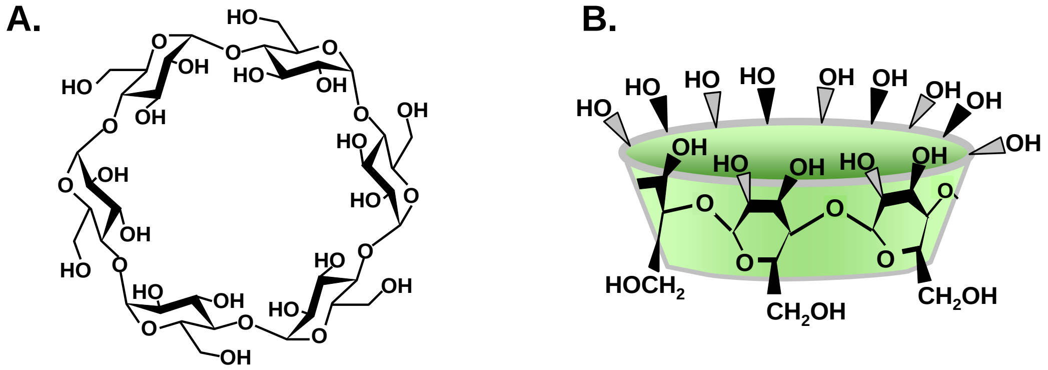

Fig. 4. A representation of the hydrophobic-hydrophilic partitioning of starch when it adopts a cyclic ("cyclodextrin") geometry. Green coloration represents a hydrophobic environment within the ring.

Composite Options for Bioplastics

The use of fibrous materials to enhance the properties of plastic matrix materials has become well established, both technically and commercially (George *et al.* 2001; Najafi 2013). Although other materials such as glass fibers and carbon fibers are more widely used as reinforcement in various plastics, cellulose-based reinforcements also are employed. The size of the reinforcements covers a huge range. At the high size end of the range, macroscopic wood pieces are used in various wood-plastic composites (Najafi 2013; Hubbe and Grigsby 2020). At the other extreme, cellulose nanocrystals, which are typically 3 to 50 nm in cross-section and 100 nm to several µm (depending on the biomass source) in length, have been used (Hubbe *et al.* 2008).

For industrial production, one of the most practical procedures to prepare a bioplastic composite involves dry-mixing, followed by melt-extrusion and compounding or injection-molding of the desired shape (Hubbe and Grigsby 2020). The relatively high temperatures and shear stress levels associated with such operations can adversely affect the resulting composites in two ways. One is a loss of molecular mass of the polymer; this issue will be considered more closely when discussing the recyclability of biopolymers and their composites. Another harm is the mechanical breakage of cellulosic reinforcement material (Teuber *et al.* 2016). As a strategy to avoid such adverse effects of high temperatures and shear stress, many studies have been carried out by dissolving the plastic in a solvent, followed by casting and evaporation (Arias *et al* 2015). The downside of solvent-casting processes can include concerns about solvent release, slower processing, and higher costs.

Compatibilization Options

Because of the generally hydrophilic nature of cellulosic surfaces, which contrasts with the hydrophobic character of PLA and other bioplastics most likely to be able to take the place of common petroleum-based plastics, it is important to consider the compatibility of the surfaces. A recent review article showed substantial increases in the strength of cellulose-reinforced plastic composites when the system contained at least one additive or surface treatment designed to improve melt-wettability or adhesion at such interfaces (Hubbe and Grigsby 2020). There are basically two approaches to achieving compatibility between a hydrophobic matrix polymer and a hydrophilic reinforcing particle – either treat the surface of the reinforcing particle or add something to (or modify) the matrix polymer. Surface modification of the cellulosic reinforcement will be considered first.

Surface derivatization

Esterification can be regarded as well suited for the modification of cellulose surfaces in the present context. Cellulosic surfaces are known have an abundance of –OH groups that will readily react with a number of modifying agents that include carboxylic acids, acid-anhydrides, or acid chlorides under suitable conditions of temperature and time. For example, it is possible to form an ester between cellulose surface –OH groups and lactic acid; such an approach has been shown to achieve better compatibility with a PLA matrix (de Paula *et al.* 2016; Hua *et al.* 2016). A related approach has been demonstrated by grafting PHB-co-valerate onto cellulose surfaces, resulting in higher mechanical performance of the PHB composites (Yu *et al.* 2014a). Even methyl esterification of cellulose surfaces has been shown to be helpful in increasing compatibility with a PHB matrix (Yu *et al.* 2014b). Zandi *et al.* (2019) showed related benefits when the cellulose surfaces were benzylated. Wei *et al.* (2017) carried out transesterification at nanocellulose surfaces with the methyl ester of canola oil fatty acids. Yin *et al.* (2020) recently demonstrated lipase-catalyzed derivatization of cellulose nanocrystal (CNC) surfaces with laurate esters, which improved the dispersion of the CNCs in PLA and increased the composite strength. Cui *et al.* (2020) treated cellulose with citric acid under conditions of 130 °C and 15 h of exposure. The citrate-reacted cellulose contributed to higher strength compared to untreated cellulose when used as a reinforcement for PLA.

Another reason why ester linkages, as just described, are well suited to the present goals is that such linkages are susceptible to enzymatic cleavage (Hasan *et al.* 2006). In other words, they could function as a weak link when the time comes for the material to biodegrade upon exposure to the environment or composting. The process depicted in Fig. 5 is based on the type of surface treatment employed by Yin *et al.* (2020).

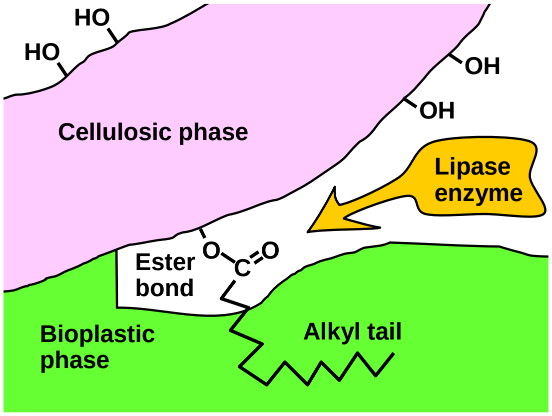

Fig. 5. Depiction of vulnerability of a class of ester bonds that were established by, and which also can be cleaved with the assistance of lipase-enzyme treatment

Other surface reactions have been reported to change the compatibility of cellulose with plastic matrix materials. These include long-chain alkyl trimethoxysilane (Orue *et al.* 2015; Hassaini *et al.* 2017; Yin *et al.* 2018; Lertphirun and Srikulkit 2019; Patwa *et al.* 2019), epoxy treatment (Kyutoku *et al.* 2019), triazine grafting (Yin *et al.* 2017), and physical coating of the cellulose with polyethylene oxide (Singh *et al.* 2020).

Reactions during compounding

As an alternative to surface derivatization, various additives or modifications can be done that involve the matrix or the mixture of reinforcing particles and bits of matrix material. A widely used version of this approach involves of adding something that is capable of reacting during melt-extruding and compounding. For instance, alkyl-trimethoxysilane has been added as an ingredient to a mixture of wood fiber and PLA prior to melt-extrusion (Pilla *et al.* 2009a,b). Quiles-Carrillo *et al.* (2018a,b) demonstrated the use of acrylated epoxidized soybean oil, which appeared to play a dual role as plasticizer and as a reagent. Maleic anhydride was used as a reagent during melt-extrusion (Rigolin *et al.* 2019). The reported results suggest that the additive reacted with the cellulose surfaces, thereby hydrophobizing the cellulose. However, a more promising version of that approach is to first react the maleic anhydride with low-molecular-mass PLA and then use the product as a compatibilizing additive (Wu 2009). The latter approach is analogous to the widespread use of maleic acid derivative of polyethylene (MAPE) as a compatibilizer for wood-polyethylene composites (Hubbe and Grigsby 2020).

Other additives

In addition to the matrix polymers, reinforcing fibers, and compatibilizing or surface-modifying treatments already considered, the processing and properties of reinforced plastic composites also can be greatly affected by such additives as plasticizers, surfactants, and polymer bends. Each of these will be considered in the main sections that follow, especially when considering how they can affect biodegradability. Even minor ingredients can be considered as potential weak links (Pillai 2014; Satti and Shah 2020), which might later be used to aid in biodegradability. For instance, when starch is used as a blend with PLA, the rate of biodegradation can be greatly increased (Leejarkpai *et al.* 2011; Mihai *et al.* 2014). In addition, hydrophobic groups appended to cellulose surfaces by means of ester linkages can serve as weak links (Wei *et al.* 2017; Patwa *et al.* 2019; Yin *et al.* 2020), since presumably such linkages can be enzymatically cleaved (Reetz 2002; Hasan *et al.* 2006).

BIODEGRADABILITY

Overview of Biodegradation Issues

Motivation for research and development of bioplastic products, such as PLA and PHB, rests partly upon a common understanding that such materials are biodegradable, and hence are likely to be more eco-friendly than synthetic polymers (*e.g.*, polyethylene) (Tokiwa *et al.* 2009). That worldview becomes threatened when it is reported that these two biobased plastics, which have shown some of the greatest promise in terms of physical properties, have failed to degrade under some conditions of soil exposure and seawater exposure (Wan *et al.* 2019a). For instance, Wadsworth *et al.* (2013) reported that when PLA was placed into the ground in the form of agricultural mulch, there was little loss of molecular mass after 29 weeks, despite some loss of mechanical strength. Relatively hot conditions of composting, *e.g.* 60 °C, have been found to give effective biodegradation of PLA, especially when employing a dialysis method (Panyachanakul *et al.* 2019). Camas *et al.* (2020) reported that seawater degradation of PLA is very slow and similar to that of high-density polyethylene (HDPE), which is well known as a persistent plastic in the environment. By contrast, on land PLA has been found to degrade about 20 times faster than HDPE.

To bring objectivity to the search for materials that biodegrade rapidly enough for practical use, governmental and international agencies have developed standards (Narayan 2012; Ruggero 2019). The following standards are for example related to compostability: ASTM D5338, ASTM D6400; ISO 14855-1, and ISO 17088:2012 (see Kale *et al.* 2007b). However, as noted by Muniyasamy *et al.* (2013), composting systems are inherently complex and difficult to standardize. For assessment of plastic biodegradation in soil, but not under composting conditions, ASTM D5988-18 or ISO 17556:2019 may be used. Biodegradability in an ocean environment can be assessed according to ASTM D6691-17. Non-floating plastic in an ocean sandy environment is covered by ISO 18830:2016 and ISO 19679:2020.

As a result of numerous studies, a general description of the main mechanistic steps of biodegradation of bioplastics can be stated (Tokiwa and Calabia 2007; Lucas *et al.* 2008; Bikiaris 2013; Muniyasamy *et al.* 2013; Wang *et al.* 2013; Pillai 2014; Elsawy *et al.* 2017; Emadian *et al.* 2017; Qi *et al.* 2017; Scaffaro *et al.* 2019; Chamas *et al.* 2020; Xu *et al.* 2020). One can envision the process happening as a series of three steps, namely (i) biodeterioration, (ii) biofragmentation, and (iii) assimilation. The last (iii) of these can include mineralization, whereby the material has been returned to the basic ingredients characteristic of soil. Qi *et al.* (2017) listed the main steps as being release of the enzyme from a microbe, followed by action of the enzymes and release of breakdown products. Factors affecting the rate of biodegradation of a bioplastic can include water uptake by the bioplastic, enzymatic attack, cleavage of ester groups, release of monomers and oligomers, diffusion of the solubilized entities, and ultimate breakdown to carbon dioxide and water (Bikiaris 2013). Hakkarainen *et al.* (2000) concluded that enzymatic degradation of PLA mainly proceeds from the chain ends rather than random scission; whereas hydrolytic degradation takes place at random locations along PLA chains. Unfortunately, the process of chain end scission or “peeling” is extremely slow and cumbersome to attain a favorable decomposition profile. In order to achieve much more effective degradation profiles, the strategy of chain cleavage is necessary. Laycock *et al.* (2017) reviewed publications suggesting that the rates of biopolymer degradation may involve both oxidative and hydrolytic mechanisms. As noted by Nair *et al.* (2017), the biodegradability of a plastic generally cannot be predicted based on its source material, such as whether it is petroleum-based or plant-based. Rather, biodegradability typically is more dependent on chemical structures, purity, and the degree to which the bioplastic forms into crystalline domains.

While most of the research attention has been focused on enzymatic routes of degradation of biopolymers, there is increasing evidence that some of the rate-limiting steps are abiotic, *i.e.* not controlled by enzymes. Already in 1998 it was observed that the rate of PLA decomposition in the temperature range of 40 to 60 °C was almost completely dependent on temperature and moisture, with little influence that could be attributed to the presence or absence of microbial enzymes (Agarwal *et al.* 1998). Copinet *et al.* (2009) and Husarova *et al.* (2014) carried out parallel experiments with and without enzymes present and found very similar biodegradation rates of PLA. Further persuasive evidence comes from a study in which PLA/starch blended materials were subjected to parallel experiments either in composting conditions or in a pile of inert vermiculite. Again, near-equal degradation was obtained in the parallel conditions. Based on an analysis of rate data, Stloukal *et al.* (2015) concluded that enzymes are unable to break down PLA until the molecular mass has been first decreased by an abiotic mechanism. Strikingly contradictory evidence, relative to other citations in this paragraph, was presented by Satti *et al.* (2017), who observed much faster degradation of PLA in the presence of certain bacteria, even allowing degradation at ambient temperature. Abiotic hydrolysis becomes significant as the temperature becomes higher than the glass transition point of PLA, which often lies within the range of 55 to 62 °C (Karamanioglu *et al.* 2014).

Though a majority of published articles have been focused on the need for more rapid biodegradation of biopolymers in the environment, it is important to maintain a balanced perspective. To perform its function, a typical polymeric material generally must remain intact for an optimized period, even when subjected to natural environments. Thus, one can use the word “tuning” to describe measures that are taken to promote or inhibit biodegradation (Gardella *et al.* 2017; Wei *et al.* 2017). For this reason, the discussion that follows will also include some findings – such as the incorporation of lignin – that often tend to slow down the biodegradation of bioplastics. Likewise, Laycock *et al.* (2017) discussed ways to determine the “safe working life” of biopolymers in diverse applications. In some applications, a persistent polymer that remains intact and can be recycled multiple times may be preferable to a biodegradable plastic, even in the case of bio-based plastics (Steinbuchel 2005).

Bioplastic Matrix Type

In the engineer’s toolkit of ways to manipulate the rate of biodegradation, perhaps the first strategy involves the selection of the type of bioplastic matrix. In general, the rates of biodegradation of the best-known bioplastics follow the order of PHB-co-valerate > PHB > PLA (Bonartsev *et al.* 2012a,b). The general rule is that greater enzymatic susceptibility can be expected for biopolyesters that have greater numbers of methylene groups within each repeating unit along the chain (Tokiwa and Calabia 2007). In addition, a higher molecular mass polymer is likely to be more durable and resistant to biodegradation (Bonartsev *et al.* 2012a). Recent work by Parisi *et al.* (2019) and Tournier *et al.* (2020) achieved very high rates of breakdown of the petroleum-based plastic poly(ethylene terephthalate) (PET) under aqueous conditions. In the case of PLA, both enantiomers are biodegradable, at least in their amorphous regions, but different enzymes are needed to initiate the biodegradation (Kawai 2010). As noted by Panchal and Vasava (2020), another option is to employ petroleum-derived monomers for the preparation of fully biodegradable plastics.

The preparation of copolymers offers additional opportunities to tune the biodegradation rates of biopolymers (Bikiaris 2013). There are innumerable opportunities to incorporate various alternative bio-based co-monomers during the synthesis (Sudesh *et al.* 2000; Kobayashi 2017). As a rule, copolymers are less likely to form highly crystalline solids, and biodegradability is generally favored by amorphous character of the thus-synthesized copolymers (Reeve *et al.* 1994; MacDonald *et al.* 1996; Tokiwa *et al.* 2009; Kawai 2010; Pantani and Sorrentino 2013; Luzi *et al.* 2015, 2019; Elsawy *et al.* 2017). For instance, Wang *et al.* (2011) described the incorporation of a weak-link monomer into polyurethane, based on the triblock oligomer PLA-poly(ethylene glycol)-PLA. Another approach, which will be considered in more detail later, is to prepare blends of different polymers (Bikiaris 2013).

Enzymes

An enzyme can be described as a relatively large protein or group of protein molecules that, on account of its structural and chemical details, is able to catalyze the cleavage or assembly of covalent bonds. Those that are relevant in terms of biodegradation of polyesters are enzymes that are excreted from the cell walls of certain fungi and bacteria (Kawai 2010). The enzymes of the greatest relevance can be classed as proteinases, lipases, esterases, and alcalases (Lee and Wang 2006; Lee *et al.* 2014; Roohi *et al.* 2018). It is important to match the enzyme with the materials and conditions. For industrial composting or bioreactors, thermophilic lipases are effective (Kawai 2010; Lee and Song 2011). Notably, poly(**L**-lactic acid) is mainly cleaved by proteases, whereas poly(**D**-lactic acid) is mainly cleaved by lipases.

Promoters of enzymatic biodegradation

Certain additives have been found to promote biodegradation of bioplastics. The list includes wood fibers (Chaiwutthinan *et al.* 2019), microcrystalline cellulose (Fortunati *et al.* 2012), sulfate-stabilized cellulose nanocrystals (s-CNCs) (Luzi *et al.* 2016), CNCs stabilized by the phosphate ester of nonylphenolethoxylate (Luzi *et al.* 2015), and benzoyl peroxide (Hu *et al.* 2018).

Inhibitors of enzymatic biodegradation

Cellulosic materials from plants, *i.e.* biomass, provides an inspiring example of achieving high strength while simultaneously being fully biodegradable in natural environments (Teeri *et al.* 2007). Cellulosic materials also will be considered in subsequent sections relative to its reported effects on the biodegradability, recyclability, and strength of bioplastic composites. Two well-known factors that tend to inhibit biodegradation of cellulose-based materials are increasing levels of lignin and increasing levels of crystallinity. An inhibiting effect of lignin on biopolymer degradation was reported by Anstey *et al.* (2014). The cited authors suggested that the slower degradation may be related to the contrasting mechanisms of degradation of the bioplastic and the lignin. Angelini *et al.* (2014, 2016) and da Silva *et al.* (2019) surprisingly found that incorporation of certain lignin types into PHB actually promoted biodegradation. However, another lignin-rich additive inhibited both hydrolytic and enzymatic degradation of the PHB (Angelini *et al.* 2014). There is widespread consensus that increasing crystallinity of the matrix polymer will slow and sometimes essentially stop the progress of biodegradation (Reeve *et al.* 1994; MacDonald *et al.* 1996; Tokiwa and Calabia 2007; Tokiwa *et al.* 2009; Bikiaris 2013; Pantani and Sorrentino 2013; Elsawy *et al.* 2017; Emadian *et al.* 2017; Seoane *et al.* 2017b).

Another type of inhibitor that affects many common enzymatic processes involves products of the hydrolysis reactions. For example, sufficiently high concentrations of lactic acid have been found to decrease rates of enzymatic hydrolysis of PLA (Panyachanakul *et al.* 2019).

In addition to favoring amorphous regions of bioplastics, hydrolytic enzymes also tend to favor attack on outer surfaces rather than bulk or internal action (Wang *et al.* 2003; Gutierrez-Wing *et al.* 2010; Arcos-Hernandez *et al.* 2012; Bikiaris 2013; Lee *et al.* 2014; Pillai 2014; Elsawy *et al.* 2017; Laycock *et al.* 2017; Ding *et al.* 2018; Chan *et al.* 2019;

Chamas *et al.* 2020). Arcos-Hernandez *et al.* (2012) concluded that the rate of biodeterioration and depolymerization was dependent on the composition of the bioplastic, its degree of crystallinity, and its surface morphology.

Accessibility

Consistent with the previous discussion, it is logical to expect that rates of biopolymer biodegradation can be increased by increasing the accessibility of biopolymer surface area to enzymes. For instance, Finelli *et al.* (1998) proposed that a blended mixture of PHB and ethyl cellulose would provide a three-dimensional accessibility to degradation that would be inherently much more vulnerable to enzymatic attack than the PHB by itself. Various researchers have suggested that faster degradation can be achieved if something is added to the mixture to allow diffusion within the bioplastic material (Fortunati *et al.* 2013; Xie *et al.* 2014; Balart *et al.* 2018; Chan *et al.* 2019). Thus, the development of cracks in the course of biodegradation (Hakkarainen *et al.* 2000; Lee *et al.* 2014; Lu *et al.* 2014; Chan *et al.* 2019) would be expected to accelerate the degradation process.

It can be hypothesized that the hydrophobic nature of various biopolymers can serve as an impediment to biological degradation processes, which invariably involves aqueous conditions. Thus, the tendency of lignin to inhibit biodegradation in some cases could be explained by the finding that its addition to PLA increased the water contact angle (Gordobil *et al.* 2015). On the other hand, one might anticipate that biodegradation would be promoted by adding materials or particles that would make the biopolymer surface more water-wettable (Seoane *et al.* 2017a,b; Turco 2019). Yamano (2014) observed a correlation between biodegradability and hydrophilicity of a polyamide, the terminal groups of which had been modified with alkyl chains having different lengths. Though there is reason to expect a general correlation between hydrophilicity and susceptibility to enzymatic attack, it is usually difficult to separate potential effects of hydrophobicity from other factors in the experimental systems.

Cellulosic materials

Cellulosic fibers stand out as a promising candidate to provide access for moisture and microbial enzymes within bioplastic composites. For example, kraft fibers are known to provide an essential wicking within cellulose absorbent products that contain superabsorbent polymers (Hubbe *et al.* 2013). Several researchers have proposed that cellulosic materials play a related role when they are present in bioplastic composites (Seoane *et al.* 2017b; Balart *et al.* 2018; Gunti *et al.* 2018; Cinelli *et al.* 2019; Lertphirun and Srikulkit 2019). By allowing access to the enzymes and aqueous media access, the hydrolysis reactions are no longer limited to the exterior of a bioplastic phase. As a further contributing mechanism, cellulosic fibers can be expected to swell when moistened (Rowell 2007), and the swelling can be expected to open up cracks within the biopolymer. Accordingly, Chan *et al.* (2019) observed the opening of channels within PHA-wood composites, allowing access for enzymatic biodegradation. Gunti *et al.* (2016) observed substantial water absorption into jute fiber-filled PLA composites. Wang *et al.* (2014) observed increased water-swelling when PLA was filled with lignin-containing nanocellulose.

A possible mechanism by which cellulosic reinforcements can facilitate entrance of water into a hydrophobic polymer matrix, as a first step in bringing about decomposition of the matrix material, is illustrated in Fig. 6. As shown, the swelling of the cellulose material, which also allows passage of water deep into the bioplastic phase, can be expected to induce cracks, depending on the brittle nature of the matrix phase.

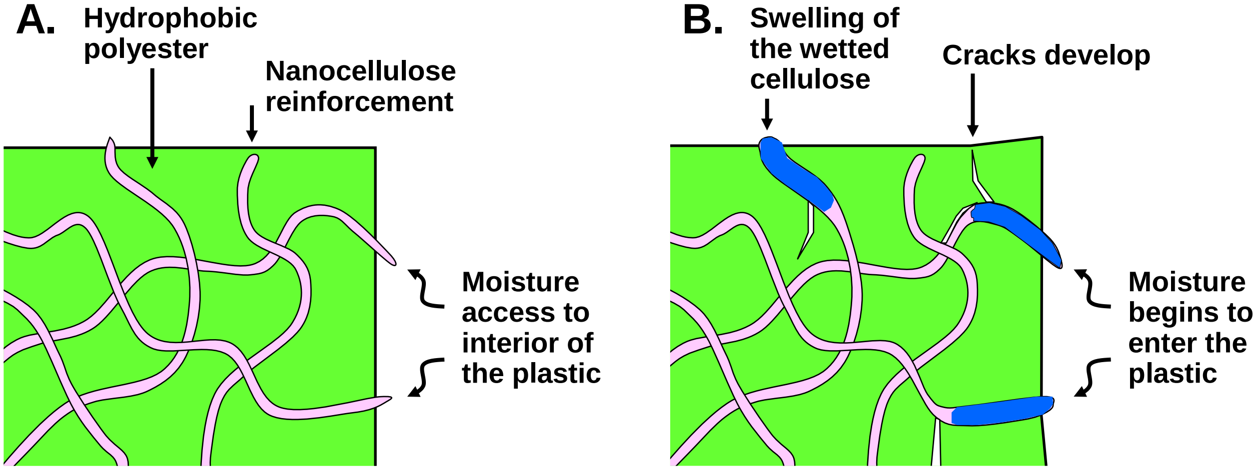

Fig. 6. Schematic diagram of (a) cellulose-based reinforcement within a hydrophobic polymer matrix; and (b) how the initial entrance of water *via* the reinforcements can lead to their swelling and possible crack formation in the matrix material

Various studies have reported positive correlations between cellulosic content in bioplastic formulations and biodegradation rates. Microcrystalline cellulose was shown to promote the biodegradation of PLA and poly(butylene adipate-co-terephthalate) (Fortunati *et al.* 2012; Giri *et al.* 2019). Lu *et al.* (2014) reported a more rapid biodegradation of PLA when formulated with distiller's dried grains and solubles. Lv *et al.* (2017) and Chan *et al.* (2019) observed increasing rates of biodegradation of polyhydroxyalkanoates with increasing content of wood flour. Several researchers have reported accelerated biodegradation of various bioplastics when formulated with cellulosic fibers (Mathew *et al.* 2005; Hidayat and Tachibana 2012; Wu 2012; Gunning *et al.* 2013; Anstey *et al.* 2014; Mihai *et al.* 2014; Gunti *et al.* 2016, 2018; Popa *et al.* 2018; Chaiwutthinan *et al.* 2019; Zandi *et al.* 2019). Yang *et al.* (2016) reported enhanced degradation of PLA films that contained lignin and cellulose. Wan and Zhang (2018) and Wan *et al.* (2019b) demonstrated rapid biodegradation of PLA that had been reinforced with poly(methylmethacrylate)-derivatized cellulose fibers. Wu (2009) observed that PLA reinforced with coconut fibers was highly biodegradable when the mixture also included maleic anhydride.

However, some other research teams observed no positive effect of cellulosic fibers on biodegradation of bioplastics (Avella *et al.* 2000). Fazita *et al.* (2015) reported that bamboo fabric reinforcement decreased the rate of biodegradation of PLA. Likewise, Masmoudi *et al.* (2016) observed a slower rate of biodegradation of PLA when formulated with cellulose fibers. Mixed results were reported by Mofokeng *et al.* (2012), who reported lower rates of PLA biodegradation when reinforced with the low level of 1% sisal fibers, but higher levels of biodegradations for combinations of higher fiber levels and time exposures of 10 days or more. Mixed results were also reported by Way *et al.* (2013) who found somewhat faster and more extensive biodegradation when the filler was cotton fibers, but the opposite when the filler was wood fibers. In summary, though the hydrophilic nature a cellulosic reinforcements might help promote biodegradation, they might also have a net effect of holding the material together more securely, thus slowing biodegradation in some cases.

Nanocellulose also has been reported to affect biodegradation rates when used as a reinforcement in bioplastics, but there was not good agreement among different studies. Urbina *et al.* (2016) incorporated PLA into bacterial cellulose by solvent casting and observed a more rapid biodegradation compared to neat PLA films. Heidarian *et al.* (2018) observed that incorporation of CNCs into recycled PLA decreased the biodegradation rates. In contrast, Luzi *et al.* (2015, 2016) observed promotional effects of CNCs on degradation of blends of PLA or its blend with PHB. However, Luzi *et al.* (2019) did not observe any important effect of CNCs on biodegradability, relative to other factors considered. Arrieta *et al.* (2015, 2016, 2018) reported that incorporation of CNCs into PLA-PHB blends did not interfere with biodegradation. It is speculated that the disagreement among studies may be related to a balance between either strengthening of the composite structure or increasing the hydrophilic nature due to the presence of the CNC.

In addition to often promoting the biodegradation of the bioplastic, another potential advantage of employing cellulose for a biodegradable composite system is the fact that cellulose itself is biodegradable. Cellulases and other wood-degrading enzymes are abundantly available in natural environments (Bhat and Bhat 1997; Mohanty *et al.* 2000; Passardi *et al.* 2005; Sukumaran *et al.* 2005; Madhavi and Lele 2009; Sharma *et al.* 2016). None of the studies involving bioplastic composites cited in this work specifically considered effects due to wood-degrading enzymes, but over a longer timeframe such effects are expected to be important, especially in soil environments and composting. The biodegradation of lignocellulosic materials in the course of composting has been reviewed elsewhere (Hubbe *et al.* 2010; Hubbe 2014).

Foam structure

Besides the use of cellulosic reinforcements, another way to invite moisture and enzymes into the interior of a bioplastic material is by creating a solid foam with an open-cell structure. Such an approach might make sense in applications where a low-density, porous material is needed. Foams have been created from PLA (Bocz *et al.* 2016; Borkotoky *et al.* 2018a,b; Zhang *et al.* 2018; Zimmermann *et al.* 2018; Sungsee and Tanrattanakul 2019), and blends of PLA and starch (Ganjyal *et al*. 2007; Sohn *et al.* 2019). In some of these cited studies the foams were reinforced with sawdust (Sungsee and Tanrattanakul 2019), cellulosic fibers (Bocz *et al.* 2016; Zhang *et al.* 2018; Zimmerman *et al.* 2018), nanofibrillated cellulose (Zimmerman *et al.* 2018), or cellulose nanocrystals (Borkotoky *et al.* 2018a,b). However, none of these cited works provided a demonstration that the formation of a foam structure affected biodegradation rates. Sungsee and Tanrattanakul (2019) demonstrated slow degradation under *in vitro* physiological conditions. Ganjyal *et al.* (2007) observed faster biodegradation of PLA foams compared to mixed PLA-cellulose acetate foams.

Effects of Exposure Conditions

Conditions during exposure of bioplastics and their composites to composting, soil, and seawater, *etc.*, have been shown to have various effects on biodegradation. Because cast-off or properly disposed plastic items can end up in widely diverse circumstances, the ideal would be to engineer suitably rapid biodegradation in each of the listed environments. Composting conditions will be considered first, since there is potentially more to learn from such studies. Not only are the conditions of composting generally better recorded than those associated with soil burial, but the effects are typically faster and more complete during the studied period.

Composting

Studies in which composting conditions were used to evaluate the biodegradation of bioplastics or their composites are listed in Table 4. As a general summary, successful composting was reported for most systems, among which PLA was by far the most widely studied. However, degradation rates appear to be sensitive to many details. One needs to keep in mind that temperature is a key variable. Successful composting under industrial conditions, which involve relative large compost piles and the generation of temperatures in the range of about 55 to 65 °C, might not imply favorable results under lower or unknown temperature conditions that are likely to prevail during household composting (Hubbe *et al.* 2010; Gorrasi and Pantani 2013; Emadian *et al.* 2017).

Table 4. Studies in Which Composting was Used to Evaluate Biodegradability of Bioplastics or their Composites

System	Findings	Reference
PLA & nanoclay	Montmorillonite promoted biodegradation.	Fukushima *et al.* 2009
PLA & blend	PLA degraded faster than cellul. acetate.	Ganjyal *et al.* 2007
PBAT & cellulose	Molecular mass loss was very slow.	Giri *et al.* 2019
PLA	Rapid biodegradation in mixed culture.	Hakkarainen *et al.* 2000
PLA	Biodegradation was sensitive to conditions.	Kale *et al.* 2007a
PLA & cellulose	Wood flour sped up biodegradation.	Mathew *et al.* 2005
PLA & others	Commercial packaging can be composted.	Musiol *et al.* 2011
PLA	Biodegradation was faster with thymol.	Ramos *et al.* 2014
PLA	Higher temperatures were successful.	Rudnik & Birassoulis 2011
PHB-co-valerate	Fibers did not interfere with composting.	Sanchez-Safont *et al.* 2016
PHB	The attack affected amorphous regions.	Seoane *et al.* 2017b
PLA & starch	The foamed material can be composted.	Sohn *et al.* 2019
PLA & fibers	Cotton fibers promoted biodegradation.	Way *et al.* 2013
Crosslinked PLA	Crosslinking hindered biodegradation.	Żenkiewicz *et al.* 2012

Hakkarainen *et al.* (2000) achieved relatively rapid biodegradation of PLA under composting conditions at 30 °C. The molecular mass decreased significantly during four weeks of enzymatic hydrolysis. Notably, insignificant degradation was observed in cases where sodium azide had been added to prevent biological processes.

Effects due to temperature during biodegradation were observed in several studies. It has been generally found that biodegradation increases with increasing temperature (Ho *et al.* 1999; Karamanlioglu and Robson 2013). Musiol *et al.* (2011) observed essentially complete degradation of PLA and other bioplastics at 70 °C. Similar results were obtained when the bioplastics were placed in distilled water at the same temperature. In other cases the researchers observed optimum temperatures for the action of certain enzymes (Lee and Song 2011; Youngpreda *et al.* 2017).

Soil conditions

Table 5 lists studies that employed soil burial tests as a means of evaluating the biodegradation of bioplastics or their composites. Striking evidence of degradation during soil burial was reported by Balart *et al.* (2018). Weight loss was minimal during an initial 14 days of soil burial at 30 °C, but thereafter there was an approximately linear loss of weight, resulting in about 80% to 95% weight loss after 42 days of burial. These results were not significantly affected by the presence of hazelnut shell flower in the PLA matrix at levels as high as 30%, though a content of 40% further accelerated the weight loss. As a general summary, many of the articles reported that biodegradation was slow, but it could be sped up by incorporating hydrophilic materials into the bioplastic. There appears to be a need for further enhancement in soil biodegradation rates of bioplastics.

Table 5. Studies in Which Soil Burial was Used to Evaluate Biodegradability of Bioplastics or their Composites

System	**Findings**	**Reference**
PHB & lignin	Lignin promoted biodegradation.	Angelini *et al.* 2014
PHB, *etc.*	Biodegradation happens at the surface.	Arcos-Hernandez *et al.* 2012
PHB-co-valerate	Degradation not affected by wheat straw.	Avella *et al.* 2000
PLA & nut shell	Plasticizer delayed biodegradation.	Balart *et al.* 2018
LDPE/PHB blend	Higher degradation seen with more PHB.	Burlein & Rocha 2015
PHB-co-valerate	Surface degradation and loosening found.	Chan *et al.* 2019
PLA blends	Blends degraded faster than pure PLA.	Chuayjuljit *et al.* 2017
PLA & lignin	10% lignin accelerated biodegradation.	da Silva *et al.* 2019
PLA & jute fiber	Soil burial gave slow biodegradation.	Gunti *et al.* 2016
PLA & grass	Weight loss increased linearly with time.	Gunti *et al.* 2018
PLA & CNC	Glycidyl methacrylate aids biodegradation.	Haque *et al.* 2017
PLA	Soil degradation was slower than compost.	Karamanlioglu & R. 2013
PLA & DDGS	Horticulture containers slowly degraded.	Lu *et al.* 2014
PLA & starch	Starch aided degradation more than wood.	Lv *et al.* 2017
PLA & PCL	Montmorillonite promoted biodegradation.	Olewnik-K. *et al.* 2020
PLA & bacteria	Bacterial inoculation was effective.	Pattanasuttichon. *et al.* 2018
PHB & plasticizer	Cellulose fibers promoted biodegradation.	Popa *et al.* 2018
PLA	There was little biodegradation in cool soil.	Rudnik & Birassoulis 2011
PLA	Bioaugmentation increased a slow rate.	Satti *et al.* 2018
PLA & PHB	Laprol decreased the biodegradation rate.	Savenkova *et al.* 2000
PHB & wood	Good biodegradability was observed.	Seggiani *et al.* 2015
PLA & bacterial	Composites degraded faster than PLA.	Urbina *et al.* 2016
PLA & chitosan	Chitosan promoted biodegradation.	Vasile *et al.* 2018
PLA mulch	There was little loss of molecular mass.	Wadsworth *et al.* 2013
PLA & straw	Composites degraded faster than PLA.	Zandi *et al.* 2019

In comparison to composting, the conditions during realistic burial in soil are often at cooler temperatures. So it is worth noting that various researchers reported slow or negligible degradation in soil tests (Rudnick and Birassoulis 2011; Karamanlioglu and Robson 2013; Gunti *et al.* 2016). In particular, Wadsworth *et al.* (2013) noted little loss of molecular mass under soil conditions; PLA mulch fabrics remained largely intact after 10 to 29 weeks of exposure. In some studies it was observed that breakdown of the bioplastic was generally limited to surface effects (Arcos-Hernandez *et al.* 2012; Chan *et al.* 2019).

Though composting and soil burial conditions have been considered most often by researchers, it seems likely that the most effective biodegradation of bioplastics will be achieved in some kind of bioreactor. For instance, Panyachanakul *et al.* (2019) reported essentially complete breakdown of PLA at 60 °C in a stirred tank with a selected enzyme and with dialysis to avoid the buildup of lactic acid byproduct. Anaerobic digestion of PHB in a mixture with municipal wastewater sludge has been reported (Gutierrez-Wing *et* *al*. 2010). Ruggero *et al.* (2019) recently reviewed the topic of biodegradation of bioplastics in aerobic composting and anaerobic digestion.

Ocean

The ocean surface represents one of the most challenging venues for the biodegradation of plastics. Figure 7 illustrates at least two ways that plastic debris can reach the ocean, even when the initial disposal might be in the form of litter or flushed items. A disadvantage of the ocean surface relative to biodegradation of bioplastics is that the prevailing temperatures are always substantially lower than those associated with successful composting of such materials. A possible positive contribution of UV light has been shown to aid in the degradation of PLA (Pattanasuttichonlakul *et al.* 2018). However, there is circumstantial evidence that floating plastic on the ocean does not necessarily remain floating (Eriksen *et al.* 2014). Cózar *et al.* (2020) proposed that much of the plastic becomes incorporated into the ocean biosphere, possibly as micrometer-sized bits. Such bits, therefore, might no longer be subject to significant UV light exposure. Indeed, the problem with radiative induction of degradation is penetration depth. Most systems that respond to light generally do so at the topmost layers, and any propagation of the radicals generated is limited to no more than a few micrometers. Therefore, UV light as a potent bioremediative agent is limited to thin materials and optically transparent (clear water) systems located at the sea surface. On the other hand, biodegradation has been shown to occur in the case of poly(ε-caprolactone) even deep within the ocean (Sekiguchi *et al.* 2011).

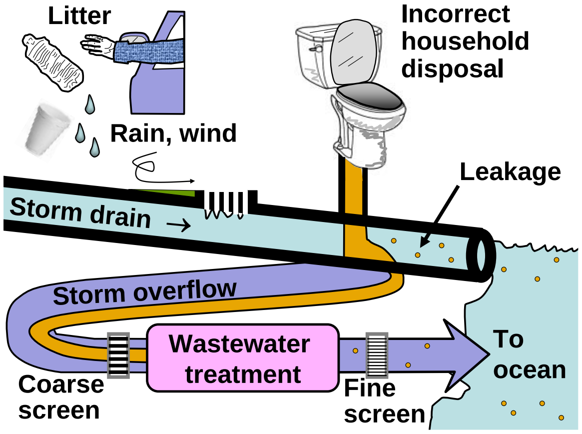

Fig. 7. Schematic illustration of ways in which plastic litter and plastic items inadvertently introduced to sewage may eventually end up in the ocean. Inspiration for the figure can be credited to https://www.cottonbudproject.org.uk/how-they-get-there.html. The content of the figure was greatly changed and all aspects were redrawn.

Water

As an alternative to biodegradation, certain bioplastic formulations containing PLA, polyethylene terephthalate, and other ingredients can be effectively degraded in distilled water at 70 °C (Musiol *et al.* 2011). The mechanism is abiotic hydrolysis, as mentioned earlier. In about a month of incubation, the two bioplastic formulations considered in the study lost about 40 to 55% of their molecular mass. Thus, one must continually keep both the abiotic and the enzyme-catalyzed pathways in mind, as well as their likely combined or synergistic effects.

Effects of Additives on Biodegradation

The formulation of a bioplastic can include many kinds of additives, and the objective of this subsection is to consider evidence of whether or not some of them tend to either promote or inhibit the biodegradation of bioplastics and related composites. Some potential additives may clearly fall into categories such as plasticizers, surfactants, coupling agents, or a component of a blended polymer matrix. However, at least some of them may straddle more than one such classification, and their roles may be described in the literature using different terms. Regardless of what category is used, the essential question is whether or not a certain additive might function as a weak link, somehow facilitating either enzymatic or abiotic degradation at the end of the material’s life.

Plasticizers

Table 6 provides key information from studies that consider the effects of various additives that can be regarded as plasticizers for bioplastics. Briefly stated, the role of a plasticizer is to increase the ability of a plastic to stretch before it breaks (Wypych 2004). Typically a plasticizer will also reduce the glass transition temperature and decrease the elastic modulus. Poly-(ethylene glycol) (PEG), in addition to acting as a plasticizer, has been reported to promote degradation of PLA (Arrieta *et al.* 2014a). In the case of PLA, an assumed plasticizing role of PEG may explain observations of faster and more complete biodegradation (Arrieta *et al.* 2014a; Xie *et al.* 2014; Zhang *et al.* 2019). The more rapid biodegradation also has been attributed to its hydrophilic nature (Xie *et al.* 2014). Faster degradation in the presence of various other plasticizers also has been reported (Nair *et al.* 2012; Carofiglio *et al.* 2017; Gardella *et al.* 2017; Yu *et al.* 2019; Zhang *et al.* 2019).

Table 6. Plasticizers and their Effects on Biodegradation of Bioplastics

System	Effect on Biodegradation	Reference
PLA-PHB & PEG	Faster disintegration in compost	Arrieta *et al.* 2014a
PLA, epoxidized linseed oil	Delayed degradation in soil	Balart *et al.* 2018
PHB, olive mill wastewater	Much faster degradation in water	Carofiglio *et al.* 2017
PLA with limonene	Slightly slower disintegration in compost	Fortunati *et al.* 2014
PLA & glycerol-PLA	Faster degradation in enzyme broth	Gardella *et al.* 2017
PLA & gum Arabic	Faster degradation with soil bacterium	Nair *et al.* 2012
PLA & polyethylene glycol	Slower degradation with soil bacterium	Nair *et al.* 2012
PLA & epoxidized oils	Increased elongation to break	Chieng *et al.* 2014
PLA & thymol	Little effect in compositing conditions	Ramos *et al.* 2014
PHB & Laprol	Slower degradation in soil	Savenkova *et al.* 2000
PLA & polyethylene glycol	Faster surface erosion in alkaline solution	Xie *et al.* 2014
PLA & three alkyl esters	No adverse effect on degradation	Yang & H. 2015
PHB & orotic acid	Faster degradation by enzymes	Yu *et al.* 2019
PLA & polyethylene glycol	Faster degradation hydrolytic degradation	Zhang *et al.* 2019

Surfactants

Because surface-active agents (surfactants) have contrasting affinities within the same molecule, it is reasonable to expect that some of them can be effective for improving the assembly process and properties of composites involving hydrophobic bioplastic matrices with cellulosic reinforcement. Bondeson and Oksman (2007) observed that an anionic surfactant helped to disperse nanocellulose (CNCs) within PLA, but the PLA matrix had lower strength as a result. Luzi *et al.* (2015) reported that addition of CNCs that had been treated with a phosphate ester of nonylphenolethoxylate promoted disintegration of PLA in compost. It is logical to expect that surfactants molecules can have the effect of increasing the amount of water molecules within a bioplastic phase, thus promoting various degradation mechanisms as already discussed.

Compatibilizers

A compatibilizer can be viewed as playing a role similar to that of surfactants, serving as a kind of bridge between otherwise non-interacting phases (Kim and Pal 2011). Often the term compatibilizer refers to polymeric species that have affinity characteristics intermediate between the main matrix polymer and the reinforcing particles (Takatani *et al.* 2008; Li *et al.* 2013). Table 7 shows cases in which use of compatibilizers (*via*, for instance, grafting of coupling agent, surface modification or use of additives) were reported to have effects on biodegradation of bioplastics and their composites. The general finding was that the additives gave rise to more rapid degradation. The effects were sometimes attributed to increased hydrophilic character of the mixture (Gardella *et al.* 2017) or faster diffusion of water (Fortunati *et al.* 2013).

Table 7. Compatibilizers and their Effects on Biodegradation of Bioplastics

System	Effect on Biodegradation	Reference
PLA & glycidylmethacrylate	Faster degradation in compost	Fortunati *et al.* 2013
PLA & PLA-polyglycerol	Faster biodegradation and hydrophilicity	Gardella *et al.* 2017
PLA & Polycaprolactone	Faster degradation in compost & water	Olewnik-K. *et al.* 2020
PLA & polyCH_3methacrylate	Faster degradation at 50 °C, pH 12.5	Wan & Zhang 2018
PLA & polyCH_3methacrylate	Faster degradation at 50 °C, pH 12.5	Wan *et al.* 2019b

Crosslinkers and coupling agents

Faster biodegradation with proteinase K of blends of PLA and poly(butylene succinate) was observed when benzoyl peroxide had been used to promote crosslinking during the composite preparation (Hu *et al.* 2018). However, it was also noted that the crosslinking appeared to resist complete degradation. Kido *et al.* (2014) likewise observed faster biodegradation of crosslinked PLA; they attributed this effect to the hydrophilic nature of the crosslinker. Lee and Wang (2006) observed lower enzyme degradability when PLA or polybutylene succinate bioplastics reinforced with bamboo fibers had been crosslinked with a lysine-based diisocyanate. Zenkiewicz *et al.* (2012) reported that physical crosslinking of PLA slowed enzymatic degradation.

Maleic anhydride, which can react during compounding, is often considered as a way to achieve better compatibility between phases in a composite. Mihai *et al.* (2014) observed high biodegradation of PLA-starch blends even with the use of maleic anhydride, which was reported to act as a coupling agent during reactive extrusion. Wu (2009) reported that PLA reinforced with coconut fibers could be degraded by bacteria at 35 °C under composting conditions whether or not the formulation included maleic anhydride.

Carboxylic Acid-bearing Compounds as Additives

There is one more kind of potential additive to consider, beyond those just discussed. Since there does not seem to be an established term for this kind of additive, it will be described here simply as "carboxylic acid-bearing compounds". Unlike the other additives already discussed, these compounds appear not to have a role in improving the processing of the material or its properties during active use. Rather, their apparent role is to promote either abiotic decomposition or a combination of abiotic and enzymatic decomposition of a biopolymer, such as PLA.

As noted by Bikiaris (2013) and Elsawy *et al.* (2017), hydrolysis of polyesters can be catalyzed by the presence of carboxylic acid groups. For instance, such groups might consist of the carboxylic acids at one of the ends of each PLA chain. Because there are more and more such groups as the molecular mass is reduced by degradation, the decomposition of PLA and related molecules can be described as autocatalytic (Tsuji and Ikada 2000; Paul *et al.* 2005; Zhou and Xanthos 2008; Elsawy *et al.* 2017). The effect was explained by Gatenholm and Mathiasson in 1994. They noted that crotonic acid released during the breakdown of PHB could lead to faster degradation of the PHB. It is possible to synthesize a PLA oligomer with pendant carboxylic acid groups and incorporate it into PLA (Stloukal and Kucharczyk 2017). The cited authors showed that at a level of just 5% in the PLA, the carboxylic acid compound was able to speed up the decomposition of PLA under both abiotic and enzyme-promoted decomposition conditions. Elsawy *et al.* (2017) suggested that the lower pH resulting from the newly formed carboxylic acid groups might be the ultimate cause of accelerated decomposition. Acidic conditions can be expected to promote the forward and reverse reactions of Fischer esterification (Vafaeezadeh and Fattahi 2015). Such an explanation is consistent with the findings of Vert *et al.* (1991). An alternative explanation might be that, on the contrary, the breakdown of PLA structure is facilitated by the deprotonation of the carboxylic acid groups, giving rise to ionized carboxylate species within and on the biopolymer. This possible mechanism is illustrated in Fig. 8. Due to the strong association between carboxylate groups and water, the bioplastic structure then would be prone to swell in water. Indeed, if the amount of carboxylation were high enough, it would be possible to prepare hydrogels from PLA-based materials (Munim and Raza 2019). An attractive aspect of this alternative explanation, if valid, is that such a mechanism would be able to work under near-neutral pH conditions, such as in the ocean (Marion *et al.* 2011) or during optimized composting (Hubbe *et al.* 2010).

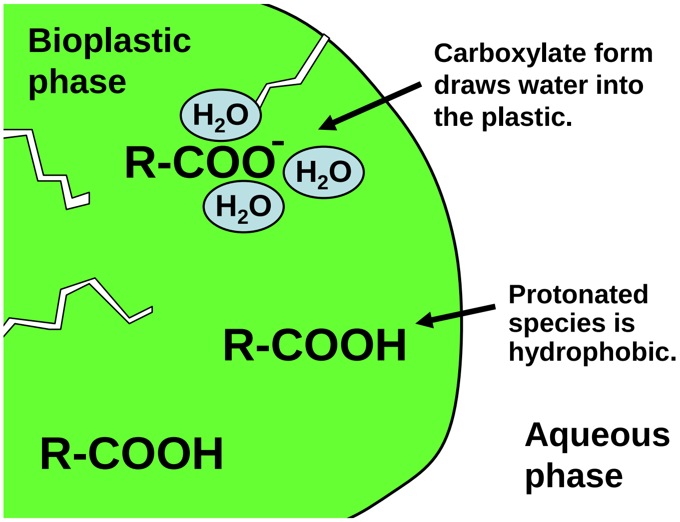

Fig. 8. Depiction of water molecules associating with the charged and highly polar carboxylate group of a carboxylic acid species within a bioplastic phase. The mechanism may depend on the presence of microcracks to allow access to water and pH values high enough to bring about dissociation (*e.g.* pH > 3.5).

In view of the effects just described, some reported effects of plasticizers, as listed in Table 6, can be considered again. It is worth noting that faster rates of degradation were observed when using the following plasticizers: olive mill wastewater residues (Carofiglio *et al.* 2017), gum Arabic (Nair *et al.* 2012), and orotic acid (Yu *et al.* 2019). The first two of these plasticizers are known to be complex mixtures, and thus the presence of carboxylic acid compounds is likely. Orotic acid has a carboxylic acid group. The cited findings support the concept that carboxylic acid groups contained within the PLA promoted its degradation. However, not all studies agree. Luzi *et al.* (2019) did not observe important effects on biodegradation rates when oligomeric lactic acid, which would be expected to have a higher carboxylic acid content, was added to PLA as a plasticizer.

Biopolymer Blends

Blending with relatively hydrophilic polymers can be a promising approach to both lower the cost of bioplastics and also to render them more susceptible to biodegradation. For instance, blends of PLA with starch have been widely reported (Martin and Averous 2001; Kalambur and Rizvi 2006; Tokiwa and Calabia 2007; Tureckova *et al.* 2008; Lu *et al.* 2009; Sarasa *et al.* 2009; Thongtan and Sriroth 2011; Nair *et al.* 2012; Mihai *et al.* 2014; Masmoudi *et al.* 2016; Elsawy *et al.* 2017; Lv *et al.* 2017; Sohn *et al.* 2019; Turco *et al.* 2019). Similarly, a blend of PLA with chitosan or cellulose acetate also was shown to allow relatively rapid biodegradation (Claro *et al.* 2016). In many of these studies, the presence of starch was shown to speed up the rate or the extent of biodegradation (Tokiwa and Calabia 2007; Tureckova *et al.* 2008; Sarasa *et al.* 2009; Nair *et al.* 2012; Mihai *et al.* 2014; Masmoudi *et al.* 2016; Lv *et al.* 2017). Some authors have attributed such effects to an overall increased hydrophilicity of the material (Pillai 2014; Vasile *et al.* 2018; Turco *et al.* 2019).

As noted earlier, when introducing starch as a potential component in a bioplastic formulation, there is evidence that by changing its molecular conformation, starch is able to present a less hydrophilic character at interfaces with hydrophobic materials (Shrimali *et al.* 2018). This attribute may help to explain why starch has shown promise as a blend in combination with much more hydrophobic bioplastics. Analogous behavior has been reported for PEG (Chen *et al.* 2002), which likewise has been employed as an additive in bioplastics, despite its being quite soluble in water.

Blends of hydrophobic bioplastics such as PLA and PHB with polymers other than starch have been widely reported. A wide range of results can be expected because of the difficulty in predicting whether a given pair of polymers, under certain conditions, will form a homogeneous melt mixture, or whether there will be separate domains of each component at a micro- or nano-scale. If two contrasting polymers are mutually soluble, then it is reasonable to expect a suppression of crystal formation (Weng *et al.* 2011), *i.e.* amorphous character, which would then suggest greater susceptibility to enzymatic degradation (Kawai 2010; Elsawy *et al.* 2017). Table 8 lists studies that compared the biodegradability of bioplastics and their blends.

Some of the effects observed relative to the biodegradability of PLA when blended with other polymers might be explained based on changes in the overall hydrophobicity, as discussed earlier. The slow biodegradability of PLA has been attributed in part to its hydrophobicity (Agrawal and Bhalla 2003; Pillai 2014). Yamano *et al.* (2014) proposed that biodegradability would be correlated with hydrophilicity. This concept is consistent with a proposed acceleration of biodegradation by hydrophilic cellulosic materials in bioplastics (Yu *et al.* 2011). Moeini *et al.* (2020) reported increased wettability of PLA with the inclusion of α-costic acid. This is an important finding because acid decomposition products during hydrolysis of bioplastics are expected to play an autocatalytic role in their abiotic decomposition, as discussed earlier. The opportunity to induce low pH in these biopolymeric media has a profound influence on the degradation profile, especially if given sufficient time and temperature. Acid is a vitally critical ally in the degradation possibilities because there is no means to buffer it in these types of polysaccharides.

Table 8. Blends among Hydrophobic Bioplastics and their Effects on Biodegradation

System	Effect on Biodegradation	Reference
PLA & PHB	Similar disintegration in compost	Arrieta *et al.* 2015
PLA & PHB	Slower disintegration in compost	Arrieta *et al.* 2014a,b
PLA & PHB	The blend degraded faster than PLA	Bonartsev *et al.* 2012a
PLA & poly(butylsuccinate)	Faster degradation in natural soil	Chuayjuljit *et al.* 2017
PHB & ethylcellulose	PHB selectively degraded	Finelli *et al.* 1998
PLA & EVA-GMA	Faster degradation in compost	Fortunati *et al.* 2013
PLA & poly(vinylacetate)	Faster degradation with methacrylate	Haque *et al.* 2017
PLA & poly(butylsuccinate)	All specimens composted well	Luzi *et al.* 2016
PLA stereo-copolymers	Amorphous films degraded rapidly	MacDonald *et al.* 1996
PLA stereo-copolymers	Amorphous films degraded rapidly	Reeve *et al.* 1994
PLA & polyCH_3methacrylate	Faster degradation than neat PLA	Wan *et al.* 2019b
PHB & cellulose acetate	Degradation controlled by composition	Wang *et al.* 2003
PHB & aliphatic polyester	Slower degradation with the blend	Yoon *et al.* 1996

Inoculation with Microbes

Though bacteria and fungi, along with their excreted enzymes, are present throughout natural environments, it is reasonable to expect that enzyme-dependent biodegradation can be accelerated by intentional inoculation or enzyme addition (Tokiwa and Calabia 2006; Satti *et al.* 2017; Satti and Shah 2020). Slower degradation has been noted in some experiments where microorganisms have been excluded (Karamanlioglu *et al.* 2014). When the bioplastic is PLA, it has been shown that certain bacterial species are most suitable, *e.g. Bacillus licheniformis*, *Pseudomonas geniculate*, *Actinomadura keratinilytica*, and *Sphingobacterium* sp. (Fukushima *et al.* 2009; Pattanasuttichonlakul *et al.* 2018; Satti *et al.* 2018; Panyachanakul *et al.* 2019; Satti *et al.* 2019). Likewise, Nair *et al.* (2016) demonstrated the biodegradation of PLA by the following fungal species: *Penicillium chrysogenum*, *Cladosporium sphaerospermum*, *Serratia marcescens*, and *Rhodotorula mucilaginosa*.

To achieve specificity in biodegradation reactions, or when conducting mechanistic studies, it can make sense to employ enzymes rather than exposing bioplastics to the bacteria or fungi that produce those enzymes (Urbanek *et al.* 2020). Table 9 lists some key results of studies involving lipase, which is especially noted as an effective agent for cleavage of the ester groups in triglyceride fats (Satti and Shah 2020). Lipase has also been reported to be efficient for cleaving ester groups in the poly-*D*-lactic acid form of PLA (Hegyesi *et al.* 2019). It should be noted that although Lee and Wang (2006) reported virtually complete breakdown of PLA, their study did not include control tests carried out without the enzymes at the same pH and temperature.

Table 9. Promotion of Bioplastic Degradation using Lipase Enzyme

System	**Effect on Biodegradation**	**Reference**
PLA & CNC	No catalytic effect for PLA breakdown	Hegyesi *et al.* 2019
PLA enantiomers	Lipase degrading poly-D-lactic acid	Kawai 2010
PLA nonwovens	Degradation producing surface cracks	Lee *et al.* 2014
PLA fibers, 40 °C	Optimum conditions for lipase hydrolysis	Lee & Song 2011
Poly(butylsuccinate)	Weight falls to zero in 10 to 20 days, 38 °C	Lee & Wang 2006
PLA, polycaprolactone	70 to 85% degradation within 12 hours	Nakajima-K. *et al.* 2012
PLA	Mass loss 28% in 50 days	Omay & Guvenilir 2014
Polycaprolact., starch	Faster degradation with increasing starch	Pranamuda *et al.* 1996
Poly(butylsuccinate)	Degradation to the cyclic oligomer starch	Tsuneizumi *et al.* 2010

Table 10 lists corresponding results for proteinase enzymes, especially proteinase K. This enzyme has been mentioned as being especially suited for PLA (Tokiwa and Calabia 2006).

Table 10. Promotion of Bioplastic Degradation using Proteinase Enzymes

System	**Effect on Biodegradation**	**Reference**
PLA & CNC	Efficient catalysis of PLA breakdown	Hegyesi *et al.* 2019
PLA/PBS blends	67% degradation of the blend in 96 h	Hu *et al.* 2018
PLA, crosslinked	Loss of physical features at 120 h at 37 °C	Kido *et al.* 2014
PLA, proteinase K	Weight falling to zero in 10 to 20 days, 38 °C	Lee & Wang 2006
PLA/PHB blends	Preferred degradation of amorphous zones	Luzi *et al.* 2019
PLA & its composites	Disintegration in less than 14 days, 37 °C	Luzi *et al.* 2015
PLA enantiomers	Strong decreases in rate with crystallinity	MacDonald *et al.* 1996
PLA, proteinase DSM	Mass loss 23% in 90 days	Omay & Guvenilir 2014
PLA, proteinase L	Preferential degradation of *L*-PLA	Reeve *et al.* 1994
PLA	Review article focusing on this topic	Tokiwa & Calabia 2006
PLA, proteinases	82% conversion at 60 °C for 24 h	Youngpreda *et al.* 2017
PLA, crosslinked	Crosslinking hindering PLA degradation	Zenkiewicz *et al.* 2012

RECYCLABILITY

Overview of Recyclability Issues

The term recyclability, when it is applied to bioplastics, can have more than one meaning. The major focus of this section will be on factors affecting the degree to which bioplastics can be melted and then formed into a next generation of plastic items. However, it is important to keep in mind that there are other alternatives, such as breaking down the materials to either oligomeric or monomeric building blocks that can be reused in some way that provides value. Various topics related to the recycling of bioplastics have been reviewed (Soroudi and Jakubowicz 2013; Niaounakis 2019; Tang and Chen 2019).

From the standpoint of overall environmental impacts, some studies have concluded that multiple recycling of bioplastics represents a favorable option, compared to other possibilities such as composting, landfilling, and incineration (Soroudi and Jakubowicz 2013; Cosate de Andrade *et al.* 2016). When the time comes that a plastic item no longer is suitable for continued use in its initial shape and dimensions, the best way to minimize usage of natural resources is to melt the plastic and reform it (Bhattacharjee and Bajwa 2017). However, Kale *et al.* (2007b) concluded that although recycling can be favorable from an energy standpoint, it is often impractical because of high requirements for cleaning and sorting. Niaounakis (2019) reported a lack of recent progress in recycling of biopolymers, although there has been patent activity, which is indicative of commercial interest in such processing of plant-derived plastics. Such activities need to be followed up by construction of suitable recycling facilities focused on bioplastics.

From a technical standpoint, it has been shown that the melt-reprocessing of PLA, PHB, and related bioplastics is feasible (Lopez *et al.* 2012; Åkesson *et al.* 2016; Lagazzo *et al.* 2019). However, there can be losses in properties of each succeeding generation of recycled bioplastic, depending on conditions of temperature, time, and shearing. The decrease of mechanical properties such as tensile strength, impact strength, and modulus, were observed in almost all studies of recycled bioplastics and composites. Two main aspects of degradation, which can take place during cycles of melting and reforming, are breakdown of the bioplastic matrix and breakdown of reinforcing particles, of which cellulosic particles are discussed in this article. Table 11 lists studies that have evaluated the properties during multiple generations of melt-reforming of bioplastics or their composites.

Table 11. Studies in Which Bioplastics or their Cellulose-Reinforced Composites Were Melt-reformed Several Times

System	Times Remade	Main Findings	Reference
PLA & cell. fibers	6	Ground cellulose/PLA recycled	Åkesson *et al.* 2016
PLA & oak fibers	6	With 30% fibers, only 6 cycles OK	Bhattacharjee & B. 2017
PLA & sisal fibers	3	Severe losses beyond 3 cycles	Chaitanya *et al.* 2019
PHB-co-valerate	3	Increasing brittleness with cycles	Lagazzo *et al.* 2019
PLA	5	No dramatic loss in properties	Lopez *et al.* 2012
Three bioplastics	7	Results depended on bioplastic type	Resch-F. *et al.* 2017
PLA, 3D printing	4	Modest degradation of properties	Cruz Sanchez *et al.* 2017
PLA & PHB-co-V	5	Large loss in molecular mass of PLA	Shojaeiarani *et al.* 2019
PHB-co-valerate	5	Moderate losses in molecular mass	Zaverl *et al.* 2012
PLA & PHB-co-V	6	PLA helped protect the PHB-co-V	Zembouai *et al.* 2014
PLA	10	Gradual loss of properties	Żenkiewicz *et al.* 2009

Breakdown of Bioplastic during Recycling

Loss of molecular mass

With respect to biopolymer breakdown during melt-reprocessing, one of the clearest indications of degradation has been shown by evaluation of molecular mass.

Table 12. Studies Evaluating Molecular Mass Changes of Bioplastics or their Cellulose-Reinforced Composites that Were Melt-reformed Several Times

System	Main Findings	Reference
PLA & sisal fibers	Hydrolysis shown by infrared spectrometry	Chaitanya *et al.* 2019
PHB & cellulose	Fibers promoting acid-induced hydrolysis	Gatenholm & M. 1994
PLA & polyester	Loss in molecular mass in 8 to10 cycles	Lopez *et al.* 2012
PLA	Large decrease in molecular mass (viscosity)	Pillin *et al.* 2008
PLA & PHB-co-V	Significant decreases in molecular mass	Shojaeiarani *et al.* 2019
PLA & PHB-co-V	Chain scission for both polymers and blends	Zembouai *et al.* 2014

Chain scission during processing leads to reduction of molecular mass, thus weakening the mechanical properties of the recycled materials. The effect is dependent on reprocessing parameters, such as temperature, time, moisture content, and number of cycles. Table 12 lists studies that have considered such changes, along with key results.

Temperature effects

Thermal decomposition has been mentioned as a likely cause or contributor to bioplastic molecular breakdown during melt-reprocessing (Gatenholm and Mathiasson 1994; Ren *et al.* 2015; Cruz Sanchez *et al.* 2017). Indeed, as will be discussed, the depolymerization of PLA upon heating can be utilized as a way to recover the monomers (Dong *et al.* 2012). According to Cruz Sanchez *et al.* (2017), thermo-oxidative degradation is a mechanism that affects thermoplastics in general, especially if the reprocessing takes place at a high temperature relative to the thermal stability properties of the polymer. Gatenholm and Mathiasson (1994) proposed that frictional heating of the bioplastic during shearing was an immediate cause of depolymerization. Vandi *et al.* (2019) recently reported that although shear during reprocessing appeared to contribute to molecular mass loss of polyalkanoates, such losses could be minimized by reducing the time of shearing and melting.

Effects of Additives on Recyclability

Plasticizers

Plasticizers, which can lower the softening temperature of bioplastics, offer a strategy to reprocess bioplastics with the prospect of lesser molecular damage. Lower glass transition temperatures of biopolymers have been observed when plasticizers were part of the formulation (Baiardo *et al.* 2003; Kulinski *et al.* 2006; Mekonnen *et al.* 2013; Fortunati *et al.* 2014; Ramos *et al.* 2014). A less brittle nature of the bioplastics in the presence of plasticizers (Jacobsen and Fritz 1999; Savenkova *et al.* 2000; Qiu and Zhou 2014; Arrieta *et al.* 2014b, 2015; Kamthai and Magaraphan 2015) also can be expected to contribute to successful processing during melt-reforming. According to Seggiani *et al.* (2015), PEG, which is a commonly used plasticizer for bioplastics, also can act as a lubricant during reprocessing.

Employment of enantiomeric pairs of biopolymers is another potential strategy that may be helpful in terms of reprocessing (Weng *et al.* 2011). This is because, especially in cases where the components are so similar that they can form an intimate mixture, the degree of crystallization within the blended matrix is likely to be less than that of a similar homopolymer. Reeve *et al.* (1994) and MacDonald *et al.* (1996) reported this kind of behavior for blends of *L*- and *D* enantiomers of PLA. Lower crystallinity generally implies greater elongation at break, *i.e.* a less brittle material. Although the cited work showed lower crystallinity in the case of blends, an opposite effect has often been reported when blending PLA with other biopolymers such as PHB (Arrieta *et al.* 2014b; 2015; 2017). In the latter cited cases, the enhanced crystallinity tends to imply that the blended components remained as separate phases, at least at a microscopic level.

Various additives during preparation of biopolymer films or composites have been shown to act as nucleating agents for the bioplastic matrix. Such effects have been reported for lignin (Mu *et al.* 2014), lignocellulose fibers (Hassaini *et al.* 2017), and nanocellulose particles (Srithep *et al.* 2013; Yu *et al.* 2014). Likewise, Yu *et al.* (2019) found that orotic acid can serve as a nucleating agent for poly(3-hydroxybutyrate-co-4-hydroxybutyrate). Thus, there will be a continual need for testing and research to better understand factors affecting the degree of crystallinity, and thus the modulus and elongational properties of bioplastics.

Strategy to repair bioplastics in the course of their recycling

In view of the expected loss of molecular mass accompanying typical melt-reprocessing of a bioplastic during its recycling, a proactive chemical approach can be used to increase the molecular mass during the processing. As shown by Beltran *et al.* (2019), the molecular mass of PLA can be increased by processing it with a chain extender and an organic peroxide. The pair of additives react with the PLA, leading to cross-linking, branching, and chain extension, which accompany some degradation reactions. Increased melt-viscosity was observed, consistent with a net increase in average molecular mass. Dhar *et al.* (2018) likewise observed increased melt-viscosity and favorable effects on properties when an organic peroxide was used during the recycling of PLA/CNC films.

Breakdown of Cellulosic Reinforcements

According to Rowell (2007), fiber breakage is a critical issue that affects the recycling of all plastic composites reinforced by cellulosic fibers. Conditions need to be selected that meet the needs for mixing while minimizing such damage. Cellulosic fiber breakage also has been observed as a result from the melt-reprocessing of biopolymer composites (Virtanen *et al.* 2016; Bhattacharjee and Bajwa 2017; Chaitanya *et al.* 2019). Figure 9 provides a pictorial representation of the expected length reduction of cellulosic reinforcing particles in the course of cycles of reprocessing.

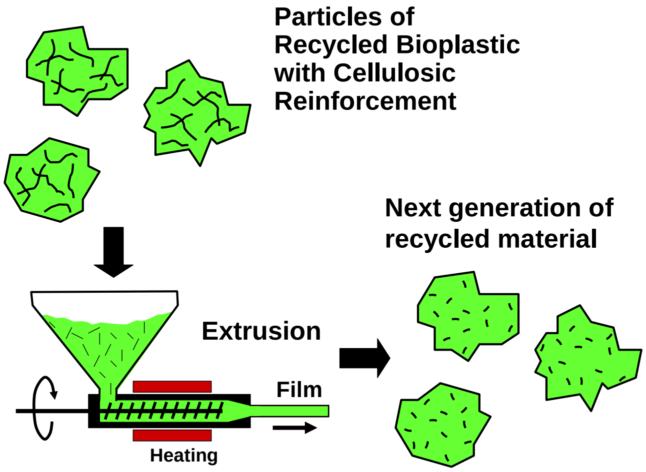

Fig. 9. Representation of breakage of cellulosic particles on account of high shear stress encountered during recycling, especially when it entails melt-extrusion

Berzin *et al.* (2017) modeled the shear forces during a melt-extrusion process, providing a way to predict the breakage of reinforcing fibers. The model was compared to results obtained with flax, hemp, and sisal fibers. Different formats of twin-screw thread pattern were employed, and the average lengths, diameters, and aspect ratios of the fibers after the extrusion process were compared. Diameter reduction generally was associated with separation of cells within the multicellular fibers. Breakage generally could be predicted by cumulative strain imparted to a fiber.

Careful adjustment of the ingoing moisture content of cellulosic fibers can be used as a strategy to minimize fiber breakage during melt-extrusion. Virtanen *et al.* (2016) showed that it was important to avoid excessive moisture levels, which can cause hydrolytic decomposition of PLA during the processing. On the other hand, the heat during the process was able to evaporate the water from moist fibers. Possibly as a result of evaporative cooling, there was less fiber cutting, as well as minimum damage to the PLA.

Recycling to Monomers and Oligomers

To complete the discussion on the recyclability of bioplastics and their composites, additional studies reporting the recovery of monomers and oligomers from PLA and other biopolymers can be cited (Dong *et al.* 2012; Soroudi and Jakubowicz 2013; Hajighasemi *et al.* 2016; Zhu *et al.* 2018). In their review of the topic, Soroudi and Jakubowicz (2013) noted that chemical recycling of PLA can be done in two ways. High-temperature hydrolysis can be used when the goal is to obtain lactic acid. Thermal degradation can be used when the goal is to obtain *L-L*-lactide. As suggested in Fig. 10, the separation of the PLA from other plastics and non-plastic substances can be envisioned to happen in two steps. First, one would expect a gross separation of the waste items into different plastic types, as well as exclusion of non-plastic items from the stream to be devoted to PLA. At a later stage, after such processes as high-temperature hydrolysis or thermal degradation, the monomers (lactic acid or *L-L*-lactide) can be purified by known methods (Ghaffar *et al.* 2014; Komesu *et al.* 2017).

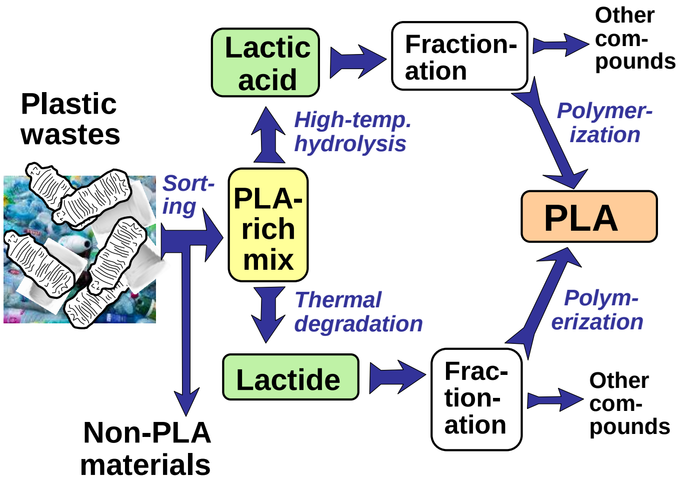

Fig. 10. Diagram suggesting two paths for the recycling of PLA by means of breakdown to monomers or oligomers followed by polymeric synthesis

Schliecker *et al.* (2003) observed that the rate of hydrolysis was influenced by the properties of PLA itself (*e.g.* molecular weight and crystallinity) as well as environmental conditions (*e.g.* temperature and pH of the reaction). Both acidic and basic conditions accelerate the hydrolysis reaction through chain-end cleavage and random ester cleavage, respectively. Studies have reported that selected catalysts (*e.g.* alkali earth metals, aluminum hydroxide, *etc.*) facilitate PLA depolymerization into *L-L*-lactide in thermal degradation, rendering an effective depolymerization at lower temperatures (Fan *et al.* 2003, 2004; Nishida *et al.* 2005). Alcohols were also used to break the ester bonds of PLA under mild conditions (Román-Ramírez *et al.* 2019, 2020). The products, alkyl lactates, are considered as valuable chemicals that can be converted into lactide and then back into PLA production. Dong *et al.* (2012) reported that the temperature required for depolymerization of PLA could be reduced by about 100 °C by use of selected catalysts. Pedersen and Conti (2017) demonstrated such processing for polycarbonate and some other polymers using hydrothermal processing. In the presence of supercritical water, the plastics were converted to a mixture of crude oil, water-soluble organic compounds, gases, and solids. Nearly 100% of conversion was obtained in the case of polycarbonate. The yield for recovery of lactic acid from PLA, however, was near zero. Payne *et al.* (2019) characterized such systems as generally having high costs, but feasible in cases where recycling to obtain lactic acid is important. Liu and his colleagues (Song *et al.* 2013, 2018) performed a serial of studies using different types of ionic liquids to depolymerize biobased polyesters. They substantially improved the efficiency of depolymerization by selecting and tailoring the ionic liquid. Overall, chemical recycling is a promising strategy because it allows the breakdown of bioplastics into monomeric products at high purity. The main issue that remains to be resolved is the cost of the process. More work needs to be done to lower the costs before commercial application.

Alternative processing routes can be considered that involve enzymatic steps. The enzyme most often reported for PLA depolymerization is protease. Hajighasemi *et al.* (2016) pursued molecular recycling of PLA by an enzymatic approach carried out for three weeks at 30 °C. In the most favorable system, about 90% of the PLA was converted to a mixture of monomers and oligomers. Tsuneizumi *et al.* (2010) showed that it was possible to separate blends of PLA and other polymers by taking advantage of differing solubilities of the components in toluene. Alternatively, the poly(butylene succinate) (PBS) in a mixture with PLA could be selectively removed by lipase, to make a cyclic oligomers that could then be reprocessed into pure PBS. Youngpreda *et al.* (2017) reported the multiple recycling of PLA using lipase at elevated temperature under nitrogen. The best results were obtained at 60 °C. Though ecofriendly, the enzymatic strategy is slow and does not necessarily satisfy the speed and scale of industrial recycling processes. It thus needs further development.

Zhu *et al.* (2018) reported the preparation of a polymer based on *g*-butyrolacone (GBL), employing a trans-ring fusion at the alpha and beta positions. The material could be converted back and forth repeatedly between its polymeric state and its monomeric state. It was also possible to tune the crystallinity of the material by blending two enantiomers, with the mixture, giving a high level of crystallinity in this case.

As noted by Ariffin *et al.* (2010), molecular recycling of bioplastics is consistent with the concept of a biorefinery operation. In an analogous manner to the refining of petroleum, a biorefinery operation employs a series of separation and reaction steps to convert a crude mixture into a diversity of relatively pure compounds, from which polymers and structures can be formed. Thus, in the cited work, copolymers related to PHB were smoothly and selectively converted into crotonic acid and 2-pentenoic acid.

Work reported by Miyoshi *et al.* (1996) provides clues to a potential recycling strategy for PLA. The cited authors were concerned about the high price of high quality PLA, which needs to have a high molecular mass. They devised a process involving continuous melt-repolymerization, using a batch-type stirred reaction and a twin screw extruder. Such a process was able to achieve a high molecular mass of PLA starting with lactic acid. It would be logical to apply a related strategy when reprocessing PLA from other sources.

STRENGTH PERFORMANCE

Overview of Strength Issues

The societal expectations for a fully successful bioplastic composite can be envisioned as a three-legged stool, of which the legs represent (1) high biodegradability, (2) suitability to be melt-pressed into recycled plastic products, and (3) strength properties that are competitive with widely used synthetic plastics. Regarding this third leg (*i.e.*, the physical and mechanical properties), much of the needed discussion already has been included in a recent review article (Hubbe and Grigsby 2020). In addition, the topic has been reviewed with a focus on fracture toughness and impact strength (Al-Maharma and Sendur 2019), processing methods used to form the biocomposites (Fortunati *et al.* 2016), surface treatments for the cellulosic reinforcements in such composites (Verma and Jain 2017), and cellulosic nanocomposites (Moon *et al.* 2011). Accordingly, the present section can be relatively brief, and readers who want to go deeper can go to the cited sources.

Matrix Attributes and Strength

When one's goal is to prepare a hard or stiff polymer that can substitute for such synthetic polymers as polystyrene or high-density polyethylene, then it makes sense to begin the process with a bioplastic having a high modulus of elasticity in its pure state. From this starting point, the final properties of the polymer can be tuned to meet a wide range of specifications, including various values of modulus, elongation at break, and other attributes, with the use of plasticizers and reinforcing particles. This situation is exemplified by PLA, the Young's modulus of which can be as high as 3300 to 4500 MPa (Jacobsen and Fritz 1999; Baiardo *et al.* 2003; Mathew *et al.* 2005; Pillin *et al.* 2008; Haafiz *et al.* 2013; Mihai *et al.* 2014; Cruz Sanchez *et al.* 2017; Kyutoku *et al.* 2019). However, unmodified PLA lacks toughness when used alone (Cui *et al.* 2020).

Effects of Additives on Physical Properties

Plasticizing agents and physical properties

Plasticizing agents can promote greater molecular mobility of segments within a polymer, thereby decreasing its glass transition temperature (Bodaghi 2020; Moeini *et al.* 2020). Related effects can include decreases in elastic modulus and increases in elongation to breakage. Though the net effects of such changes can sometimes be hard to predict, plasticizers provide a tool by which technologists can adjust the properties of bioplastics to meet different goals, such as toughness and strength.

In the formulations of bioplastics, various plasticizers have been shown to decrease the glass transition temperature (Jacobsen and Fritz 1999; Baiardo *et al.* 2003; Mekonnen *et al.* 2013; Fortunati *et al.* 2014; Patwa *et al.* 2019; Moeini *et al.* 2020; Panaitescu *et al.* 2020). Likewise, increased elongation before breakage has been reported when adding plasticizing agents to PLA and other bioplastics (Jacobsen and Fritz 1999; Mekonnen *et al.* 2013; Cheng *et al.* 2014; Kamthai *et al.* 2015; Patwa *et al.* 2019). Jacobsen and Fritz (1999) reported that a large proportion of 10 wt% of PEG was required in order to achieve large increases in the elongation ability of PLA.

A surprising, but widely reported effect of certain plasticizers has been increases in the rate or extent of crystallinity of PLA and some other bioplastics. Because crystallinity implies a loss of polymer segment mobility, such an effect can be regarded as contrary to the classic functions of a plasticizer. Such behavior was reported in the following studies (Li and Huneault 2007; Arrieta *et al.* 2014a; 2018). Similarly, Arrieta *et al.* (2017) reported that PHB was able to act as a nucleating agent when blended with PLA. Li and Huneault (2007) reported that the addition of acetyl triethyl citrate and PEG as plasticizers made it possible to achieve good crystallinity within PLA even when cooling was rapid. The opposite tendencies of plasticization and inducement of higher crystallinity are illustrated schematically in Fig. 11. It would appear that an enhanced mobility of polymer segments at a critical stage in processing may be important to allow the crystallization process to occur, which is essentially the opposite of plasticization.

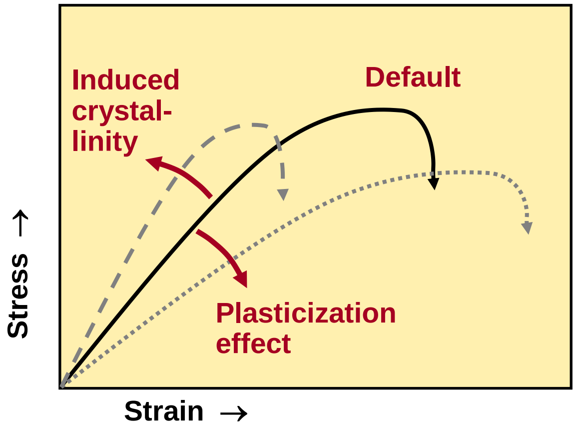

Fig. 11. Schematic description of two key effects on a typical stress-strain curve of plastic material: increases in crystallinity induced by the additive, *vs.* plasticizing effects

Polymer blends and strength

Typical plasticizing agents are monomers, and that fact can raise concerns related to leaching or uncontrolled/unwanted diffusion. In the case of the well-known plasticizer bisphenol-A, leaching from petroleum-based plastics has been tied to endocrine disruption effects (Rubin 2011). Leaching can be minimized by such means as increasing the molecular weight of the plasticizing agent, or even by covalently bonding it to polymer segments (Bodaghi 2020). Both toxicity and leaching issues need to be kept in view when formulating plasticization systems for the next generation of plastic materials, especially in food-contact and biomedical/pharmaceutical applications.

The ultimate manifestation in increasing the molecular weight of a plasticizer is to blend a bioplastic with another biopolymer. For example, Qiu and Zhou (2014) showed that poly(ethylene adipate) was very effective at the 20% level in increasing the elongation to breakage of PLA. Effects of PEG and poly(ethylene oxide) (PEO) (same polymer, but with a higher molecular mass and usually, a different route of production) likewise can be regarded as both plasticizers and potential blend components in bioplastics (Jacobsen and Fritz 1999). Oguz *et al.* (2019) achieved high toughness when recycled polyurethane was bended with PLA.

Effects of Cellulose Reinforcements

Cellulose fibers

As tabulated by Hubbe and Grigsby (2020), there is abundant evidence that cellulosic reinforcement in bioplastics can be used as a way to increase the elastic modulus. Published articles considered in the cited source clearly show that the effect was not sensitive to whether the reinforcing particles were large (*e.g.* cellulose fibers or wood particles) or very small (*e.g.* cellulose nanocrystals). In a broad sense, these results are consistent with a high elastic modulus of the crystalline regions of cellulose and the high aspect ratios of typical cellulose-based reinforcements, *e.g.* 138 GPa (Nishino *et al.* 1995). Some examples of cellulose fibers-reinforced PLA or PHB composites, with increased Young's moduli, are given in the following articles (Huda *et al.* 2005a,b, 2006; Ludvik *et al.* 2007; Pilla *et al.* 2009a; Tawakkal *et al.* 2010; Mofokeng *et al.* 2012; Gunning *et al.* 2013; Way *et al.* 2013; Battegazzore *et al.* 2014; Lu *et al.* 2014; Mihai *et al.* 2014; Rapa *et al.* 2014; Ren *et al.* 2015; Gunti *et al.* 2016, 2018; Masmoudi *et al.* 2016; Liu *et al.* 2017; Sanchez-Safont *et al.* 2018; Wan and Zhang 2018; Dehghan *et al.* 2019; Vandi *et al.* 2019; Wan *et al.* 2019b; Panaitescu *et al.* 2020).

Nanocellulose

Because of the higher costs and additional processing steps required to prepare very small cellulosic reinforcing particles and to ensure their compatibility with the matrix polymer, it is important in each application to consider what might justify such costs and efforts. Nanocellulose can provide clear advantages if the product needs to be transparent or if the melted material needs to flow through extremely small nozzles. Relatively large cellulose particles might be expected to act sometimes as defects in a plastic film or structure, possibly providing a site for initiation of a crack or tear. On the other hand, as discussed in an earlier section, one needs to consider whether those same "defects" may play an important role in promoting more rapid biodegradation in cases where biodegradability is a recognized goal.

With respect to strength of plastic composites in general, the benefits of nanocellulose addition have been clearly shown in multiple studies (Hubbe and Grigsby 2020). However, relatively few studies have reported strength gains that could clearly be attributed to the presence of nanocellulose in a bioplastic matrix. Seoane *et al.* (2017a) prepared PHB-CNC composites using a solvent-casting procedure, which is an excellent way to avoid degrading cellulosic reinforcements. Higher strength was achieved. Srithep *et al.* (2013) reported nearly a two-fold increases in tensile modulus when poly(3-hydroxybutyrate-co-3-hydroxyvalerate) was reinforced by nanofibrillated cellulose. Wang *et al.* (2014) observed increases in tensile strength of PLA when composites were formed with lignin-containing cellulose nanofibers, using a solvent-casting method. Yu *et al.* (2014) achieved superior strength when CNCs were hydrophobized by the grafting of PHB-co-valerate onto their surfaces. In that form, they were able to increase the Young's modulus of PHB-co-valerate by 95% at a 20% loading. Yin *et al.* (2017) achieved increases in both tensile strength and elongation to breakage when using lipase-mediated surface hydrophobization of CNCs to reinforce PLA.

Several authors have reported that nanocellulose was able to promote crystallization of the biopolymer during cooling. This is an important effect due to an expected relationship between the modulus of a polymer and its crystallinity (Humbert *et al.* 2011). The following studies reported evidence that nanocellulose was acting to promote crystallization of PLA or PHB-co-valerate (Yu *et al.* 2011; Srithep *et al.* 2013; Mu *et al.* 2014; Wang *et al.* 2014; Almasi *et al.* 2015; Arrieta *et al.* 2015; Hua *et al.* 2016; Hassaini *et al.* 2017; Borkotoky *et al.* 2018b; Seoane *et al.* 2019). Avella *et al.* (2000) reported a similar enhancement of crystallinity when ordinary wheat straw fibers were used during melt-extrusion of PHB-co-valerate.

Compatibilizers and strength

The importance of achieving compatibilization at the interface between cellulosic reinforcements and oleophilic polymers was one of the most consistent findings that emerged from an earlier review of the literature (Hubbe and Grigsby 2020). Such effects were observed with high statistical certainty in a large number of studies, spanning a wide range of sizes of reinforcing particles. The following studies showed such effects in the case of PLA and other oleophilic biopolymers (Yu *et al.* 2014; Almasi *et al.* 2015; Orue *et al.* 2015; de Paula *et al.* 2016; Hua *et al.* 2016; Wei *et al.* 2017; Yin *et al.* 2017, 2018, 2020; Kyutoku *et al.* 2019; Cui *et al.* 2020; Singh *et al.* 2020).

CONCLUDING STATEMENTS

Based on the publications considered in this review, it is clear that considerable progress has been achieved in the preparation of bioplastic composites that have more rapid biodegradability at the end of life, melt-recyclability when recycled, and strength characteristics during their use. Strategies that have been demonstrated for different systems can be regarded as a tool set for future development work. An overall strategy to achieve the three goals of high biodegradability, retention of properties during melt-reprocessing, and improved strength characteristics during its use can be summarized briefly as follows:

1. As a first step in any project aimed at achieving a biodegradable plastic that also meets high strength requirements, it is recommended to start with a high purity and high molecular mass biopolymer such as poly(lactic acid) or poly(hydroxybutyrate)-co-valerate having a sufficiently high elastic modulus to meet the overall needs for the intended application.
2. Employ cellulosic reinforcing particles that have been selected to have a suitable size, depending on the needs of the final product. Cellulosic fibers of natural size can be used, except if the product requires very high smoothness, transparency, or ability to flow through tiny openings, *etc.*
3. Use an effective chemical treatment to achieve sufficient compatibility between the surfaces of the cellulosic particles and the bioplastic matrix, especially in cases where the latter has a hydrophobic nature. For example, cellulosic fibers can be hydrophobized by esterification to be more compatible with PLA. Select a surface treatment system than can be readily reversed by enzymatic effects when the material is composited or if it ends up in a natural environment.
4. Employ a “poison pill” strategy, at an optimized level, to help initiate an eventual autocatalytic breakdown of PLA or related biopolymers when placed into a natural environment or composting. For instance, this can be done by formulating PLA with PLA oligomers, the molecular mass of which determines the frequency of carboxylic acid groups.
5. Employ a plasticizer during formulation of the material as a means of either promoting crystallization during cooling of the bioplastic or as a strategy to increase elongation before breakage. Because the two effects can work against each other, it is

recommended to try several types of plasticizers over a range of dosages and processing conditions to seek optimized effects.

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