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Hydrolytic degradation of polylactic acid (PLA) and its composites

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ABSTRACT

Biodegradable polymers are seen as a potential solution to the environmental problems generated by plastic waste. In particular, the renewable aliphatic polyesters of poly(hydroxyacid)-type homopolymers and copolymers consisting of polylactic acid (PLA), poly(glycolic acid) (PGA), and poly(*e*-caprolactone) (PCL) constitute the most promising bioresorbable materials for applications in biomedical and consumer applications. Among those polymers, PLA has attracted particular attention as a substitute for conventional petroleum-based plastics. PLA is synthesized by the fermentation of renewable agricultural sources, including corn, cellulose, and other polysaccharides. Although some of its characteristics are disadvantageous (e.g., poor melt properties, mechanical brittleness, low heat resistance, and slow crystallization), there exist potential routes to resolve these shortcomings. These include copolymerization, blending, plasticization modification, or the addition of reinforcing phases (e.g., chitosan (Cs), cellulose, and starch). In this review, we discuss the degradation mechanisms of PLA and its modified form in the environment, current issues that hinder the achievement of good Cs/PLA combination, and ways to overcome some of these problems. Furthermore, our discussion is extended to cover the subjects of hydrolytic degradation and weathering effects with different Cs/PLA blends.

1. Introduction

As various industries attempt to lessen their dependence on petroleum-based fuels and products for economic and environmentally sustainable development, a major focus has been shifted to biopolymers as alternatives to synthetic and non-degradable materials. Today, about 50% of packaging products are made up of plastic materials produced mostly from fossil fuels [1]. After these products are used, they are discarded into the environment and subject to slow degradation. Consequently, an enormous amount of discarded packaging is excluded from natural recycling. In light of the associated environmental problems, the management of plastic waste is an important environmental issue [2].

There is an urgent need for the development of biodegradable materials that can be degraded in an environmentally-friendly manner over a relatively short time. In this framework, bio-based polymers can play an important role because, unlike conventional plastics, they can help reduce emissions of toxic and greenhouse gases (e.g., carbon dioxide). Additionally, the production and use of biodegradable polymers can help control the ever-increasing depletion rate of fossil fuel resources [3].

Biodegradable polymers can be classified into four categories depending on their type of synthesis and source, as shown in Table 1 [4,5]. The first category of biopolymers is generated from biomass such as agro-polymers from agro-resources including polysaccharides and proteins [6]. Polysaccharides are largely limited to starch and cellulose derivatives for practical applications in plastics or as water-soluble polymers. Both of these materials are composed of D-glycopyranoside repeating units, which produce products with very high molecular weights and thousands of units. Structurally, the starch's repeating unit is poly(1,4-α-D-glucopyranoside) [7], whereas the repeating unit of cellulose is poly(1,4-β-D-glucopyranoside) [8]. This difference in structure can be used to control the biodegradation rates and properties of the polymers. Proteins may be a better option because they are found in nature; they are not soluble or fusible without decomposition [9]. Proteins are widely used as fibers in different forms, including wool, silk, and gelatin (collagen), and are useful for encapsulation in the pharmaceutical and food industries. Their structure includes an extended chain of amino acids joined through amide linkages, which can readily be degraded by enzymes (especially protease).

The second category of polymers, i.e., polyhydroxyalkanoates (PHAs), is obtained by microbial production routes. PHAs are aliphatic polyesters that

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Table 1
Classification of biodegradable polymers [4,5].

Or.	Category	Group	Example
1-	**Polymers from biomass**	Polysaccharides	– Starches (wheat, potatoes, maize) – Cellulosic and ligno-cellulosic products (wood, straws, etc.) – Others (pectins, chitosan/chitin, gums)
		Protein and lipids	Animals (casein, whey, collagen/gelatin) Plants (zein, soya, gluten)
2-	**Polymers obtained via microbial production**	Polyhydroxyalkanoates (PHA)	– Poly(hydroxybutyrate) (PHB) -poly(hydroxybutyrate-co-hydroxyvalerate (phbv)
3-	**Polymers chemically synthesized using monomers obtained from agro-resources**	Poly(hydroxyacid)	– Polyglycolic acid (PGA) – Poly(lactic acid) (PLA)
4-	**Polymers chemically synthesized from fossil fuel resources**	Aliphatic co-polyesters Aromatic co-polyesters Others	Poly(butylene adipate-co-terephtalate) (PBSA) Poly(butylene succinate adipate) (PBAT) Polycaprolactones (PCL), polyesteramides (PEA)

are naturally produced via a microbial process in a sugar-based medium; they act as carbon and energy storage materials in bacteria [10,11]. They were the first biodegradable polyesters utilized in plastics. Aliphatic polyesters are the most easily biodegraded synthetic polymers. In the third category of biodegradable polymers, monomers from agro-resources are used to synthesize products like poly(*a*-hydroxy acid) and polyglycolic acid (PGA), which have been successfully used in medical applications as biodegradable sutures. Polylactic acid (PLA), obtained from di lactide, also has a wide range of applications in medical and industrial sectors. The last category of biodegradable polymers is obtained from non-renewable resources. Synthetic polymers are gradually being replaced with biodegradable materials, especially those derived from natural resources (due to their biodegradability). Recent innovations in edible and/or biodegradable polymer films have been widely discussed in the literature, presenting improvements in food packaging, surgery, and pharmaceutical applications [12–14].

PLA is thermoplastic aliphatic polyester that is generally derived from agricultural products. It has several attractive properties such as its biocompatibility, high strength, stiffness, and thermo-plasticity; however, it does have low impact strength. Due to its commercial availability at an affordable cost, PLA has been extensively studied and used for packaging applications. It has also been utilized in biomedical applications including sutures, bone screws, and tissue engineering scaffolds [15,16].

A lot of research has contributed to widening the application range of PLA through chemical and physical modifications. For instance, chitosan (Cs) can be used to modify PLA to extend its range of application to medicine, edible packaging or coatings, food additives, cosmetics, water treatment, and antifungal agents [17,18]. Chitosan and PLA have different surface chemistries; PLA is hydrophobic while chitosan is hydrophilic. In many instances, incompatibility issues between the components of the composite material may result in an inferior interface that does not adequately transfer stress to the load-bearing filler. Moreover, the lack of miscibility can be a challenge when attempting to form homogenous blends.

As a renewable and sustainable resource, polylactic acid has a great potential for reducing the dependence of the petroleum-based materials for economically and environmentally-sustainable development. In this review, we discussed the significance of its hydrolytic degradation along with the overview on the chemical structure and many attractive properties. The modification of PLA, the blends of PLA with other renewable and sustainable biopolymers, and the parameters influencing the degradation process have also been described. As indicated by the compiled information, different research attempts have been made to produce suitable combinations of PLA and Cs, both chemically and physically. Thus, the influence of these combinations on the degradation of PLA or Cs by different types of degradation mechanisms, such as hydrolytic degradation and weathering, has also been explored.

2. Chemical structure of PLA and its properties

In the family of biodegradable polymers, PLA is one of the most frequently used polyesters. This is mainly due to its many favorable properties, including its easy availability, relatively good strength, biocompatibility, and biodegradability [19–24]. PLA can be prepared by direct condensation of lactic acid or by the ring-opening polymerization of cyclic lactide dimers. Because the direct condensation route is an equilibrium reaction, difficulties removing trace amounts of water in the later stages of the polymerization generally limit the ultimate molecular weight that is achievable by this approach. Mitsui Toatsu Chemicals has patented an azeotropic distillation process using a high-boiling point solvent to drive the removal of water in the direct esterification process to obtain high-molecular weight PLA [25]. Ring-opening polymerization is also a widely used technique [26–28].

Chemically recycling PLA into its monomer is crucial for the regeneration and re-synthesis of this renewable resource, thereby limiting the environmental impacts associated with its production and disposal. Additionally, the production of PLA from recycled components allows for substantial energy savings compared to using virgin raw materials; depolymerization via hydrolysis leads to the production of high-quality lactic acid, which can be used to reproduce high-quality PLA. This avoids the expensive and complex process of glucose fermentation, which is commonly used to obtain virgin lactic acid [29,30]. As PLA is generally subject to the environmentally-safer degradation into its monomer (i.e., lactic acid), it can be applied to various biomedical fields (e.g., resorbable sutures and implants for orthopedic surgery).

As PLA exhibits unique properties comparable to PET or polypropylene (PP) (i.e., polyolefin), it has been used preferably in a broad range of applications. This range is due to its ability to be stress crystallized, thermally crystallized, impact modified, filled, copolymerized, and processed with most polymer processing equipment [31]. It can be formed into transparent films or fibers. Furthermore, its injection and blow-moldable preforms can be used for the preparation of PET-like bottles. PLA also has excellent organoleptic characteristics, making it useful for food contact and related packaging applications. Although the cost of PLA production is currently high relative to conventional petroleum-derived plastic products, its ever-increasing demand and production volumes may change its expense with time [22].

3. Processes and factors controlling the hydrolytic degradation of PLA

The chain cleavage reaction during the hydrolytic degradation of PLA proceeds preferentially in amorphous regions, which leads to an increase in the polymer crystallinity [24]. Following chain scission, the