



# Hydrolytic degradation of polylactic acid (PLA) and its composites

Moataz A. Elsaywy<sup>a</sup>, Ki-Hyun Kim<sup>c,\*</sup>, Jae-Woo Park<sup>c</sup>, Akash Deep<sup>b,\*</sup>

<sup>a</sup> Polymer laboratory, Petrochemical Department, Egyptian Petroleum Research Institute, Nasr City 11727, Cairo, Egypt

<sup>b</sup> Central Scientific Instruments Organisation (CSIR-CSIO), Sector 30C, Chandigarh 160030, India

<sup>c</sup> Department of Civil and Environmental Engineering, Hanyang University, 222, Wangsimni-Ro, Seoul 04763, Korea

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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( $\epsilon$ -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- $\alpha$ -D-glucopyranoside) [7], whereas the repeating unit of cellulose is poly(1,4- $\beta$ -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

\* Corresponding authors.

E-mail addresses: [kim61@hanyang.ac.kr](mailto:kim61@hanyang.ac.kr) (K.-H. Kim), [dr.akashdeep@csio.res.in](mailto:dr.akashdeep@csio.res.in) (A. Deep).

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

Or.	Category	Group	Example
1-	<b>Polymers from biomass</b>	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-	<b>Polymers obtained via microbial production</b>	Polyhydroxyalkanoates (PHA)	– Poly(hydroxybutyrate) (PHB) –poly(hydroxybutyrate-co-hydroxyvalerate (phbv)
3-	<b>Polymers chemically synthesized using monomers obtained from agro-resources</b>	Poly(hydroxyacid)	– Polyglycolic acid (PGA) – Poly(lactic acid) (PLA)
4-	<b>Polymers chemically synthesized from fossil fuel resources</b>	Aliphatic co-polyesters Aromatic co-polyesters Others	Poly(butylene adipate-co-terephthalate) (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( $\alpha$ -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

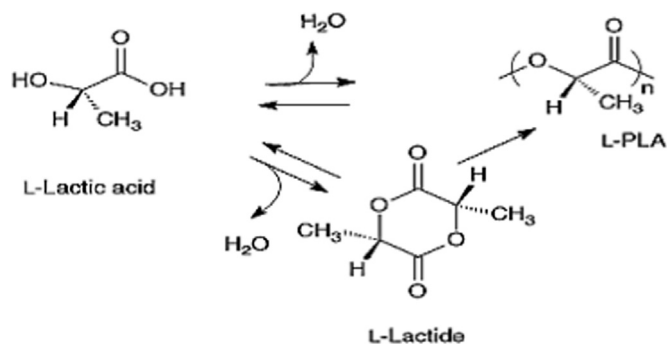


Fig. 1. Polymerization degradation routes for polylactic acid [80].

carboxylic end groups act catalytically to affect the hydrolytic degradation of PLA in a self-catalyzed and self-maintaining process [32–34]. This hydrolytic degradation proceeds heterogeneously: it is faster inside the molecular structure than on the surface [34–36]. This mechanism was assigned to the internal autocatalytic effect of the carboxyl end groups. Fig. 1.

In aqueous solutions, the hydrolytic degradation of PLA proceeds via random cleavage of the ester bond, which is controlled by four basic parameters: the rate constant, the amount of absorbed water, the diffusion coefficient of chain fragments within the polymer, and the solubility of degradation products [37].

In general, the hydrolytic degradation of PLA-based solid polymer matrices can proceed through under two different mechanisms: (i) surface or heterogeneous reactions and (ii) bulk or homogeneous erosion [38]. Differences associated with the principles of these contrasting mechanisms are illustrated in Fig. 2. The former type of degradation generally proceeds much faster than that of the latter type. It is thus found that the hydrolytic degradation of bulk amorphous poly(D, L-lactic acid) devices should proceed heterogeneously while it occurs faster at the inner parts than at the surface. As such, its autocatalysis may exert more influence in the interior [39].

The following two observations were recognized with the progress of degradation. Firstly, degradation tend to increase the number of carboxylic acid chain ends known to autocatalyze ester hydrolysis. Secondly, only soluble oligomers in the surrounding aqueous medium are found to escape from the matrix. Before the completion of degradation, the soluble oligomers closer to the surface can be leached out, while those in the core of the matrix remain entrapped. As the latter fraction starts to degrade into lactic acid, it will lead to the reduction of pH in the core [40].

The effect of pH on the hydrolytic degradation of PLA has been studied in a few reports. Lyu and Untereker (2009) studied the

hydrolysis of PLA in THF solutions with nominal pHs varying from 0 to 14. They reported the slowest reaction rate at pH 4 ( $K_2 = 1.11 \times 10^{-11} \text{ M}^{-1} \text{ s}^{-1}$ ). Because the  $pK_a$  of lactic acid is 3.84 [41], solutions with  $pH > 4$  will have lactic acid that is mainly in a dissociated form, thereby accelerating hydrolysis. Alternatively, in solutions with  $pH < 4$ , lactic acid at the chain ends exists in an associated acid form, which can also accelerate the hydrolysis reaction via auto-acceleration [42]. Göpferich also investigated the dependence of PLA degradation on the pH of the medium [43]. They reported that a fast rate of degradation can be realized at both low and high pH conditions. Fast chain scission at low pH explains the heterogeneous erosion of PLA due to autocatalysis. The generated monomers, which are carboxylic acids, accelerate polymer degradation by further lowering the pH [44].

#### 4. Parameters influencing the degradation mechanism of PLA

Albeit the complexity, the degradation of semicrystalline PLA matrices can be accounted for by two stages [45]. Firstly, random hydrolytic scission of ester bonds proceeds with the diffusion of water into the amorphous regions. As the degradation proceeds, the degree of crystallinity tends to increase. In the next stage, hydrolytic attack occurs from the edge towards the center of the crystalline domains with the degradation of the major portions of the amorphous area. According to the analysis of the hydrolytic degradation of monodisperse lactic acid oligomers, such process took place by chain-end scission at low pH values [39]. Alternatively, lactoyl lactate split off in alkaline media. The -OH end group was important in the hydrolytic degradation, as its rate was reduced with the blocking of -OH. The hydrolysis was also affected sensitively by such variables as the temperature and pH conditions of the solution [46–48].

The degradation of D, L-lactic acid oligomers was investigated at varying pH conditions (e.g., 1.5, 4.5, and 7.4) at  $65^\circ\text{C}$  [37]. The hydrolytic rate was dependent on the molecular weight of the oligomer along with pH and temperature of the media. The degradation rate at two extreme pH conditions (1.5 and 7.4) was higher than that at 4.5. The mode of the reaction was chain-end cleavage under acidic conditions, while the degradation proceeded via random ester cleavage under basic conditions. Although degradation becomes a bulk process above  $T_g$ , it is restricted to the surface below such temperature [46]. In addition, the increase of gamma-irradiation dose on biopolymers was also seen to reduce the onset time for degradation [49].

It is acknowledged that the degradation of PLA is critical for controlled release systems (e.g., drug delivery). Hence, The occurrence of surface and bulk erosion, combined with the autocatalytic effect of carboxyl groups, is likely to distort the even rate of release or the zero order release that is important for controlled release [50]. Moreover, as the diffusion of drugs can take place through the polymeric matrix, it may add more complexity in association with the swelling characteristics of the polymeric matrix. In addition, weight loss was also recognized as an important parameter of degradation, although the effect of such conditions can be experimentally validated after the completion of the reaction. Other parameters used to monitor the degradation process include the loss of mechanical strength of the polymer matrix and the reduction in the molecular weight. In particular, the latter property can be evaluated by means of gel permeation chromatography (GPC) or by conducting intrinsic viscosity measurements [51]. Polymers can be degraded by random chain scission to lower the  $M_w$  of small chains. Since only the monomer degradation products (i.e., lactic acid) are soluble, very large reductions in both the  $M_w$  and mechanical strength typically occur before a decrease in the weight of the sample is observed.

Monitoring the weight loss can be of analytical significance, as stated above, but it is not particularly effective in “real world” applications where real-time assessment of the degradation rates is desired. Consequently, a number of techniques (e.g., mechanical,

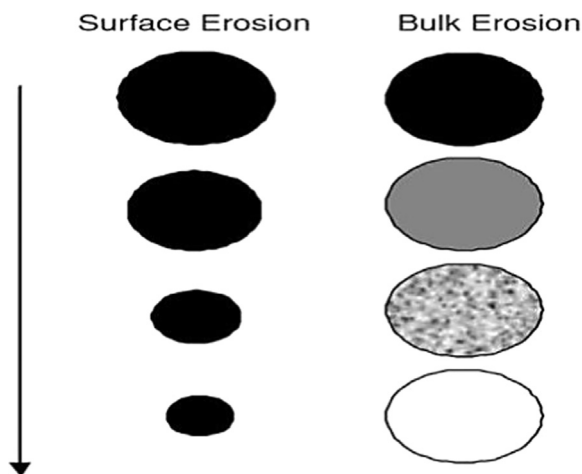


Fig. 2. Mechanisms of hydrolytic degradation in polymers [38].

thermal, morphological change, and spectral methods) can be used in parallel to determine significant pieces of real-time information. Such combined information can provide reasonable characterization for the overall process of polymer degradation.

It has also been noted that the crystallinity of PLA tends to increase as it degrades. This can be attributed to the fact that hydrolytic chain cleavage proceeds preferentially in the amorphous regions, resulting in an increase in the polymer's global crystallinity [52]. Thus, determining the crystallinity of a sample before and after degradation can also be used as a supplementary tool to assess the progress of degradation. Radiolabeling has also been suggested as an effective method for this purpose [53,54], but this approach has yet to attract much attention.

## 5. Modification of PLA

PLA is one of the most commonly used biodegradable biopolymers in medical and food packaging applications. However, if one considers the practical requirements of packaging in engineering and medical systems, PLA has many obvious limitations. For instance, the slow degradation rate of PLA cannot satisfy a wide range of application-specific requirements [55]. From a medical point of view, there are no cell recognition sites, which are important for tissue compatibility on the surface of PLA for tissue engineering applications. Additionally, because PLA is strongly hydrophobic and can elicit an inflammatory response from the tissues of living hosts, it has low affinity with cells when it is used as a tissue engineering material. Alternatively, the standalone use of PLA directly as a packaging material does not circumvent the problem of brittle breakage. It is, therefore, of industry interest to improve the mechanical performance of PLA in order to meet industrial requirements. In this context, plasticizing, blending, and other types of modifications have been proposed to enhance the degradability, mechanical strength, and physical and bioproperties of PLA. Several researchers have reported approaches that can be used to modify the hydrophilicity, degradability, and breaking elongation of PLA [56–58].

As PLA is a synthetic polymer made from natural resources, earlier stages of modification with other polymers can be carried out via copolymerization. The copolymerization of lactide with other lactone-type monomer polyglycolides can improve PGA's crystallinity, melting point, and solubility. Thus, the copolymerization product (poly-lactide-glycolic acid (PLGA)) exhibits better properties than PLA and PGA [59].

Plasticizing is an important modification strategy that can be used to improve the mechanical properties of PLA. Elsayy et al. [60] used jojoba oil as a natural plasticizer for PLA. The selection of jojoba as a plasticizer for PLA was based on the solubility compatibility of both of these materials. The plasticizing effect of jojoba oil on PLA was determined through mechanical testing. The results revealed an improvement in the elongation and impact strength properties of PLA-jojoba as compared to neat PLA [60].

Some other types of modifications for PLA include the formation of its biodegradable composites with microcrystalline cellulose, wood fibers, wood flour, cellulose fibers, and cellulose nanowhiskers [7–9]. Kowalczyk et al. [61] prepared and examined PLA composites with electrospun cellulose nanofibers. They evaluated the effect of a significant decrease in the size of the pure cellulose fiber on the composite properties. They reported that the mechanical properties could be significantly improved by mixing a certain percentage of nanofibers into the composite [61].

In addition to all of these types of modifications, the bulk properties of PLA can also be modified by blending it with other materials. Blends of PLA with various synthetic and biopolymers have been prepared in an effort to enhance the properties of PLA. When compared to the neat polymer, PLA blends with collagen, poly(butylenes succinate adipate), poly(hydroxybutyrate-valerate), poly(ethylene glycol), poly(methyl methacrylate), polyethylene, poly(ethylene oxide), and poly(butylenes

adipate-co-terephthalate) have been reported to improve the properties. The toughness, modulus, impact strength and thermal stability have all been improved [62,63]. However, in some cases, PLA composites with different natural fibers demonstrate lower overall material strengths, as compared to native PLA; this is due to the poor interfacial adhesion between the filler and the matrix [64]. PLA brittleness, with less than 10% elongation at breakage and low toughness, restricts its applications [65]. Despite the fact that its tensile strength and elastic modulus are similar to those of poly(ethylene terephthalate) (PET) [66], its poor toughness limits its utilization in applications that require plastic deformation at higher stress levels (e.g., screws and fracture fixation plates).

PLA/Cs combinations are regarded as promising compounds due to the synergistic addition of the attractive properties of both materials. Cs is a rare alkaline polysaccharide in nature; it is actually the deacetylated product of chitin, which is natural cellulose-like biopolymer found mainly in the exoskeleton of marine animals (e.g., shrimp, crabs, and lobsters) [67]. The chemical structure of chitosan is very similar to that of cellulose; with the exception that one  $\text{NH}_2$  group replaces an OH group on the glucose molecule. However, Cs is only soluble in dilute acidic solutions and its mechanical properties are rather poor. Furthermore, Cs degradation may be a slow process, especially when it is used as a scaffold material [68–71]. The above issues limit the broader applications of Cs. Alternatively, PLA has excellent mechanical properties and processability with an adjustable degradation rate.

### 5.1. Chitosan/PLA composites

As alkalescence of Cs can effectively neutralize the acidic product of PLA, the PLA/chitosan composite should be more biocompatible with their complementary characteristics. Note that the acidic degradation products generated by PLA can be neutralized by Cs, while the mechanical properties (especially the brittleness of the high crystallinity) of Cs can be improved by the presence of PLA. Nonetheless, an effective blending between them is still a challenge in the following two respects. First, due to a high glass transition temperature, Cs start to decompose before melting [72]. Moreover, co-solvent that is good for both Cs and PLA has not yet been found. Cs can only be dissolved in a few types of dilute acidic aqueous solutions, while PLA can typically be dissolved in organic solvents. Although many efforts have been made to blend PLA with Cs, only a few of these have been successful. Even in these cases, some obvious phase separation was observed in the blends [73–75].

### 5.2. Types of chitosan/PLA blends

A good deal of efforts have been put to synthesize PLA-chitosan composites to realize the advanced properties of such composites. However, due to the aforementioned difficulties in such synthesis, some modifications were made to incorporate two materials in two different forms (one in nanoparticle form and the other in the polymer matrix). Some chemical reactions have been proposed as a suitable solution for this problem, e.g., different PLA grafting techniques with chitosan, including a direct grafting method (DG) and a ring-opening polymerization method (ROP) (Fig. 3) [76]. Differences in the properties of the products obtained from these methods were distinctive. The copolymer obtained by DG is more thermostable than the one obtained by the ROP method. Economically, direct grafting is more suitable for a large industrial scale because D, L-lactic acid is far less expensive than L-lactide. Unfortunately, they found that the grafted chitosan is not soluble in the organic solvents of PLA or in dilute acid, which is a good solvent of pure chitosan.

In one study, Zhang and Cui investigated how grafting lactic acid (LC) onto the amino groups in Cs (PCLA) affected enzymatic degradation and hydrolytic degradation in a buffer solution [77]. In vitro and in



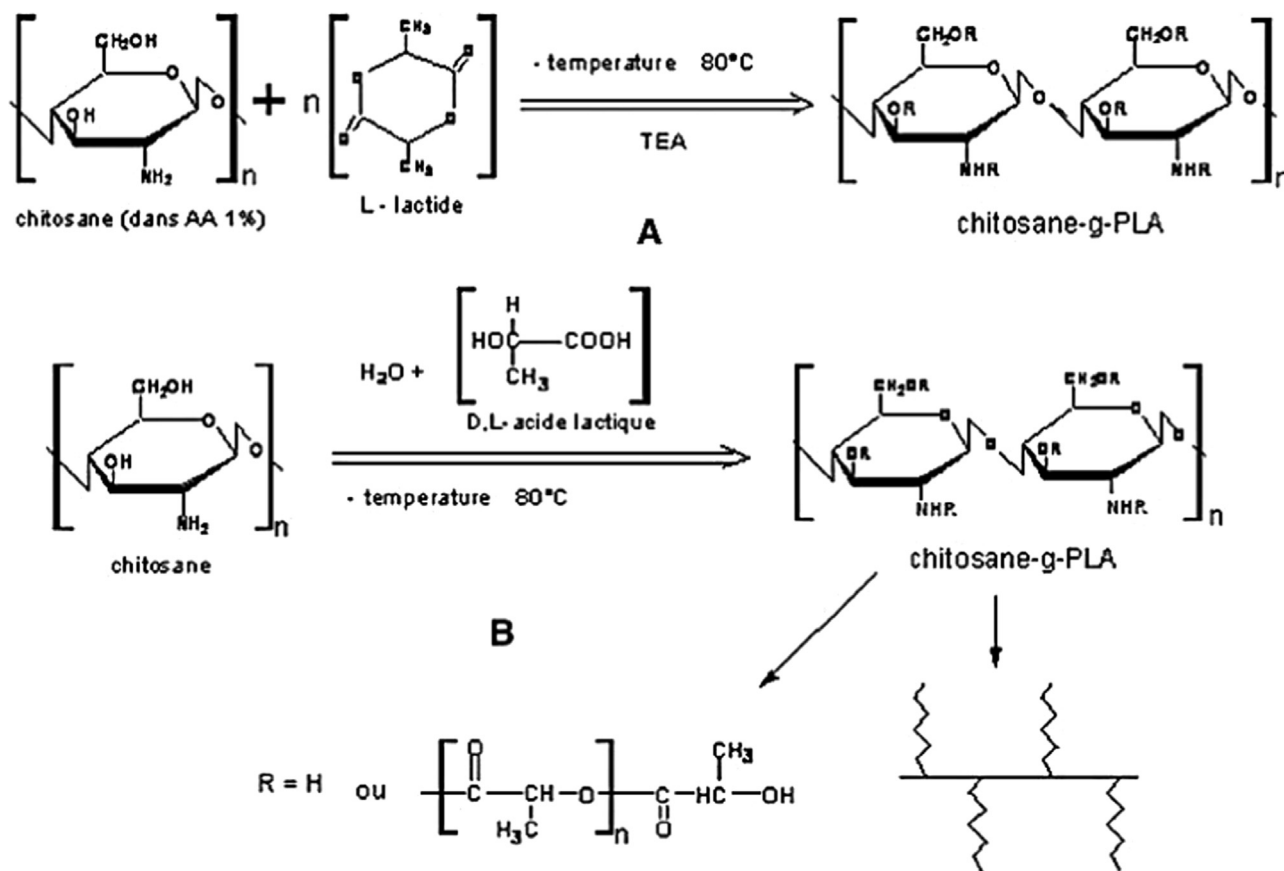


Fig. 3. Synthesis of chitosan-grafted PLA copolymers: (a) by ROP and (b) by DG [76].

Table 2

Hydrolytic degradation of chitosan, PLA, and its compounds [77].

Order	Sample name	LC/Cs (wt/wt)	Weight loss in vitro	Weight loss in vivo	pH
1	Chitosan	–	43, 3	58	7.7
2	PLA	–	27, 4	16.67	7.1
3	PCLA-I	2	50	64	7.5
4	PCLA-II	3	60	70	7.5
5	PCLA-III	4	70, 5	77	7.8

- In vitro incubation in PBS with the addition of 4 mg/mL lysozyme solution.
- In vivo scaffolds subcutaneously implanted onto the backs of Kunming mice.
- The pH value in PBS by sodium azide (0.01 wt%) at 37 °C.

vivo weight loss during a test period of 16 weeks and the effect of a medium pH are summarized in the following table.

The data from this table reveal that the degradation of grafted compounds of PCLA was faster and more significant than those of neat Cs and PLA. All of the PCLA copolymer samples quickly lost mass

Table 3

Effect of degradation on the physical properties of PLA/Cs and PLA/Kr/CS [79].

Type	Kr	Cs	Young's modulus		Impact strength		Elongation at break (%)		Tensile strength at break (MPa)		TGA weight loss (%)	
			0 h	600 h	0 h	600 h	0 h	600 h	0 h	600 h	0 h	600 h
PLA	–	–	2587.3 ± 25.0	2424.7 ± 23.0	11.0 ± 0.3	4.1 ± 0.4	3.8 ± 0.3	1.0 ± 0.2	58.6 ± 1.3	13.1 ± 0.2	97.3	97.98
PLA/Cs	–	30	2906.1 ± 30.0	1970.7 ± 12.0	6.7 ± 0.5	4.8 ± 0.3	2.2 ± 0.4	0.6 ± 0.1	49.5 ± 2.0	10.0 ± 0.5	96.2	95.51
PLA 1	4	–	3258.6 ± 13.0	–	11.1 ± 0.2	–	1.3 ± 0.2	–	65.1 ± 1.5	–	–	–
PLA 2	2	30	2482.7 ± 11.0	1010.8 ± 21.0	8.3 ± 0.3	5.7 ± 0.7	1.8 ± 0.1	0.9 ± 0.1	38.1 ± 1.3	8 ± 0.3	92.0	91.89
PLA 3	4	30	2272.2 ± 36.0	1116.4 ± 18.0	8.0 ± 0.2	8.0 ± 0.4	1.6 ± 0.2	0.9 ± 0.1	35.8 ± 1.2	5.0 ± 0.2	97.6	93.95

because of the hydrolysis of the grafted lactic acid (Table 2). Hydrolyzed lactic acid promoted the degradation of Cs, which also led to an increase in the pH of PCLA; the pH showed wave characteristics. Meanwhile, the mass loss ratio became faster. However, PLA showed very little mass loss or pH change, which may be linked to its higher molecular weight (as compared to the grafted portion in PCLA compounds) (Table 3).

As another strategy, crosslinkers were used to synthesize Cs/PLA blends in order to impart stability against hydrolytic degradation. This may prove useful for different purposes, such as for wound dressing applications. Ignatova et al. prepared water-resistant hybrid nanofibers based on Cs and PLA by crosslinking nanofibrous mats with glutaraldehyde vapor. The importance of this crosslinked blend was derived from its antibacterial activity toward gram-positive and gram-negative bacteria [78].

The effect of weathering on Cs/PLA blends and the influence of adding keratin into the blend were studied [79]. They compared the blend before and after accelerated weathering. Under weathering conditions, some ruptures in the PLA matrix took place with a poor

response to mechanical stress when the action of some variables (humidity, temperature, and UV light) was put together. The most extreme drop-off was observed from neat PLA in terms of mechanical performance over time. However, in case of the composite materials, the expected behavior is not guaranteed. As the modulus data did not show evidence of chain scission of the PLA, some changes are expected to occur in the interactions between chitosan and PLA and/or between keratin (Kr) and PLA/chitosan. The hydrophilic character of Cs allowed the penetration of water inside the polymer matrices, which accelerated the hydrolytic degradation of Cs-containing blends. The following table summarizes the main observations of the above work [79].

## 6. Conclusions

Biopolymers made from renewable resources are important and innovative materials because they are expected to minimize our dependence on fossil fuel-based polymers. They can reduce the amount of waste that is produced due to their biodegradable nature (in contrast to conventional petroleum-based polymers). PLA is considered to be one of the most promising biopolymers due to its advantageous chemical structure and physical properties, which make it suitable for many applications. Hydrolytic degradation of PLA is an important property for a variety of applications, such as drug delivery and food packaging. Erosion and bulk degradation are the two possible mechanisms that determine the degradation of polymers. The degree of degradation of PLA also depends on the ability of water to diffuse into the polymer matrix and the temperature. As a reference, the degradation of the PLA polymer matrix is restricted to its surface if the temperature remains below the  $T_g$  value. As per literature reports, the pH, temperature, and autocatalytic behavior of PLA are the main parameters that control the degradation process. The degradation is very fast at highly basic and highly acidic mediums (as compared to neutral conditions). A number of methods have been used to track the progress of the degradation process, but the use of a combination of these analytical techniques seems to be the most effective strategy for characterizing the overall degradation process. The properties of PLA can be enhanced by certain modifications. Mixing with Cs has been shown to influence the degradation of PLA. However, the mutual miscibility of Cs and PLA still need to be improved to obtain efficient PLA/Cs blends. Chemical modifications and the physical application of other nanocomposites are also suitable options.

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