

Degradation of Graft Polymer and Blend Based on Cellulose and Poly(L-lactide)

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ABSTRACT: Degradable polymers were prepared by blending and graft polymerization of cellulose and poly(L-lactide) (PLLA). The cellulose/poly(L-lactide) blends and cellulose-graft-poly(L-lactide) polymers were characterized by FTIR, NMR, DSC, and TGA. Wide-angle X-ray powder diffraction (WAXD) and degradation tests [by alkaline, phosphate-buffered saline solution (PBS), and enzyme solution] showed changes in the crystalline structure as a result of degradation. The results indicated that blending and graft polymerization could affect crystallization of the polymers and promote the degradability. The polymers with low degree of crystallinity showed higher degradability. In contrast, enzyme, alkaline, and PBS degraded material decreased rate of polymers degradation. In addition, high levels of PLLA resulted in a decrease in degradation. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2013

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INTRODUCTION

Renewable natural biopolymers are being studied and produced to reduce our dependence on non-renewable petroleum-based materials. Cellulose is a highly interesting biopolymer due to its renewability, low price, high availability, and good mechanical properties.^{1,2} However, there are also some challenges to the chemical modification of cellulose because of its high molecular weight, high crystallinity, rigidity of backbone chain, and insolubility. Green solvents, for example, ionic liquids 1-*n*-butyl-3-methylimidazolium chloride (BmimCl)^{3,4} and 1-allyl-3-methylimidazolium chloride (AmimCl)⁵ has received great attention recently as reaction media of cellulose. Several articles were available on the physical and chemical properties of modified cellulose and the relationship with degradation.^{6–9} PLLA is a non-toxic and compostable biopolymer to CO₂ and water.¹⁰ PLLA has seen applications in biomedical materials (degradable sutures, drug delivery systems, and temporary scaffolds for tissue).^{11–14}

The grafting and blending of synthetic polymers to natural polymers can lead to materials with unusual and useful properties for a variety of applications. Polymer blending could be a convenient and inexpensive method to develop novel polymeric materials. Cellulose modified by blending method and polymerization in ionic liquids which could improve some of the unfavorable properties of cellulose, such as moldability and degradability. Cellulose graft polymerization may be an approach to modify function cellulose.^{15–17} Ring-opening

polymerization (ROP) could be an effective method of synthesizing aliphatic polyesters, which could lead to the control of general material properties, including degradability.^{18–20}

Huda et al.²¹ prepared recycled cellulose/PLA composites by extrusion followed by injection molding. Miyamoto et al.²² examined tissue biocompatibility of cellulose and its derivatives in two *in vivo* tests. The *in vivo* absorbance in living tissue was found to depend on the degree of crystallinity and the chemical structure of the sample. Teramoto and Nishio had also summarized their study on cellulose acetate-based graft polymers.^{23–25} It was found in experiments that the growth rate of spherulites in crystallized polymers was much lower than that of PLLA in crystallization. So, it was assumed that if the cellulose was blended or grafted with an amount of PLLA, low crystallinity materials might be obtained, which may contribute to the performance of degradation.

In this study, we prepared cellulose-graft-poly(L-lactide) polymers and cellulose/PLLA blends. The products were detected by FTIR and NMR spectroscopy. Degradability of the materials was determined using hydrolytic and enzymatic hydrolysis conditions. This study was aimed at providing properly information on basic cellulose/PLLA polymer synthesis.

EXPERIMENTAL

Materials

Microcrystalline cellulose [MCC; degree of polymerization (DP) of 255] and *N*-methylimidazole (99%) was supplied by the J&K

Chemical Reagent Co., China. Allyl chloride (98%) was purchased from Acros Organics. 1-Allyl-3-methylimidazolium chloride (AmimCl) was synthesized according to the literature.⁵ L-Lactide (L-LA, 98%) was purchased from A Johnson Matthey Co., UK. 4-Dimethylaminopyridine (DMAP, 99.5%) was provided by Haili Chemical Industry Co. Poly(L-lactide) (PLLA; M_w 50,000 g/mol) was purchased from Jinan Daigang Biomaterial Co.. Trichloromethane (99%) was purchased from Beijing Chemical Works. Lipase L3126 from porcine pancreas was supplied by Beijing Solarbio Science and Technology Co..

Preparation of Cellulose/PLLA Blend

PLLA and MCC were dried in a vacuum oven at 80°C for 24 h before processing and extended at 100 rpm with a single-screw extruder (PLE330 Brabender OHG, Duisburg, Germany, 475 mm length, L/D of 25) at 183°C for 10 min. The polymer melt was transferred after extrusion through a preheated cylinder to a mini injection molder.

Preparation of Cellulose-g-PLLA

Based on previous experiments,^{26–28} a typical polymerization procedure was employed as follows. 4% (w/w) MCC/AmimCl solution was first prepared by mechanical stirring at 80°C under nitrogen for 1 h in a dried Schlenk tube; then L-LA, DMAP were added into the tube and mixed till dissolved, the tube was degassed in vacuum/N₂ in 1 h cycles (three times); finally, the reaction was kept at 90°C under nitrogen with vigorous stirring for 9 h; after cooling to room temperature, the resultant polymer was precipitated with deionized water, and then the polymer was dissolved in toluene to obtain a purified graft polymer. The purified polymer was dried in a vacuum oven at 60°C till a constant weight.

Hydration of Cellulose/PLLA Blend and Cellulose-g-PLLA

The water uptake capacity of each cellulose/PLLA blend and cellulose-g-PLLA was determined by the hydration in deionized water at 37°C. The sample (200 mg, in triplicate) was placed in deionized water for a required period of time. Within this interval, after blotting the surface water with a piece of filter paper, hydrated samples were taken and weighed immediately.

Alkali and PBS Hydrolysis

Specimens were put in vials filled with pH 14.00 alkaline liquor and pH 7.40 phosphate-buffered saline solution (PBS), respectively, sealed and heated to 37°C and the specimens were cleaned and weighed periodically.

Evaluation of Degradability

Specimens (250 mg) and PBS (25 mL; pH 7.40) were placed in a conical flask with lipase (25 mg). The mixture was incubated at 37°C for a specified time, and then enzyme solution was diluted 200 times and absorption measured using a spectrophotometer at 210 nm. The concentration of lactic acid in solution was obtained based on the standard curve: $c \text{ (g/L)} = A/0.6298$, where A is the UV absorbance at 210 nm. The weight loss of the polymer was calculated from the formula: $\text{weight loss\%} = (c \times 5000)/250 \times 100$, where c is the concentration of lactic acid in solution.

Analytical Instruments

FTIR spectroscopy (Magna-IR 750, Nicolet, USA) was used to chemically characterize the cellulose/PLLA and cellulose-g-poly(L-lactide) materials using a KBr pellets.

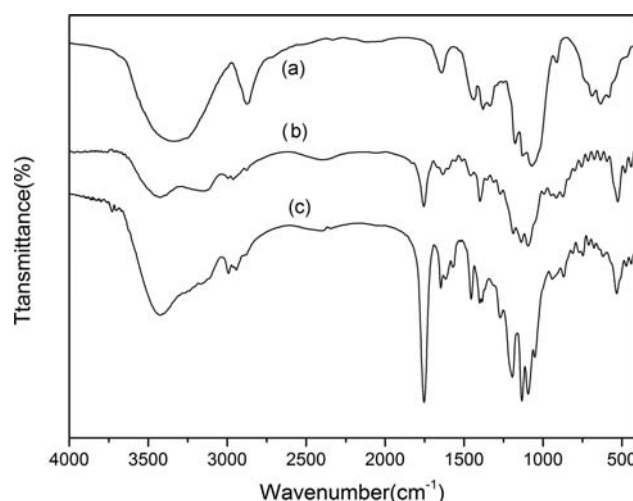


Figure 1. Fourier transform infrared spectra for (a) cellulose, (b) cellulose/PLLA blend, and (c) cellulose-g-PLLA.

¹H-NMR spectra of cellulose-g-PLLA polymer was recorded on a Bruker AV400-MHz NMR spectrometer (Bruker, Germany). Deuterated dimethyl sulfoxide (DMSO-*d*₆) was used as the solvent with a drop of trifluoroacetic acid-*d* to shift active hydrogen to lower field area, and tetramethylsilane (TMS) as an internal standard.

WAXD was performed by XRD-6000 X-ray diffractometer (Shimadzu, Japan) using Ni-filtered Cu K α radiation (40 kV, 30 mA) with 4°/min scanning rate at room temperature. Diffraction intensity was measured in a range of $2\theta = 5\text{--}40^\circ$.

Differential scanning calorimetry measurement was carried out on a Q100 instruments (TA instruments) equipped with a refrigerated cooling system, an indium standard was used for calibration. The samples were first heated from 20 to 280°C at the rate of 10°C/min under nitrogen to erase any previous thermal history before being rapidly cooled to 20°C in 6 min, then the samples were subsequently heated at 10°C/min to observe the second heating scan.

Thermogravimetric analysis (TGA) was carried on a Q50 thermogravimetric analyzer (TA instruments) with a heating rate of 10°C/min from 20 to 700°C under nitrogen.

Ultraviolet analysis was carried out on UV2000 spectrophotometer (UNICO, China).

RESULTS AND DISCUSSION

Preparation of Cellulose/PLLA Blend and Cellulose-g-PLLA

To confirm the changes in chemical structure of the cellulose/PLLA blend and cellulose-g-PLLA, FTIR spectroscopy was performed. Figure 1 shows the FTIR spectra of (a) cellulose, (b) cellulose/PLLA blend, and (c) cellulose-g-PLLA. The strong bands at 3423 cm⁻¹ [Figure 1(b)] and 3425 cm⁻¹ [Figure 1(c)] were assigned to the OH stretching mode of cellulose.^{29,30} The PLLA modified cellulose resulted in the strong ester carbonyl adsorption at 1751 cm⁻¹ [Figure 1(b)] and 1753 cm⁻¹ [Figure 1(c)]. This implies that the amount of PLLA was blended or grafted on cellulose.^{7,31} The above two mentioned peaks exist in cellulose/PLLA blend and cellulose-g-PLLA, which confirmed

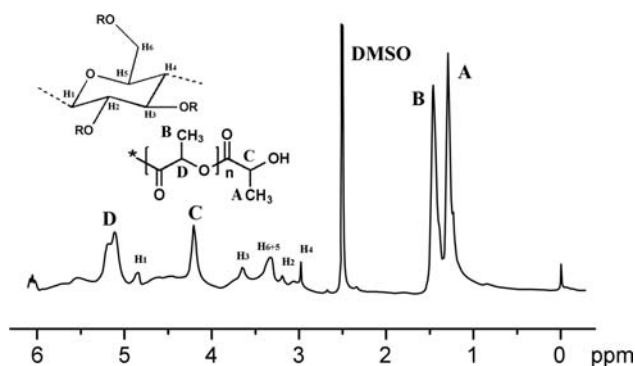


Figure 2. ^1H -NMR spectrum of cellulose-g-PLLA ($\text{DP}_{\text{PLLA}} = 3.15$) in $\text{DMSO}-d_6$.

the introduction of the PLLA into the cellulose by blending method and graft polymerization.

^1H -NMR spectroscopy was performed of cellulose-g-PLLA ($\text{DP}_{\text{PLLA}} = 3.15$) was shown in Figure 2. In the spectrum, an area from the terminal methyl protons of lactyls was labeled A, an area from terminal methyl protons of lactyls in PLLA side-chains was labeled B, an area from terminal methine protons of lactyls in PLLA side-chains was labeled C, a resonance peak area derived from internal methine protons of lactyls in PLLA side-chains was designated as D.^{32–34} The degree of lactyl substitution (DS) was defined as the average number of hydroxyls substituted for lactyls per anhydroglucose residue of cellulose and the molar substitution (MS) was defined as the average number of introduced lactyl units per anhydroglucose residue of cellulose. The average degree of polymerization of the PLLA-side chain (DP_{PLLA}) which was equal to the molar amounts of combined LA per glucopyranoside unit of cellulose-g-PLLA was estimated directly by ^1H -NMR analysis according to the following equations:

$$\text{MS}_{\text{PLLA}} = \frac{\text{lactyl units}}{\text{anhydroglucose units}} = \frac{\text{IA}_{(a+b)}/3}{[\text{IA}_c - \text{IA}_{(a+b)}/3]/7} \quad (1)$$

$$\text{DS}_{\text{PLLA}} = \frac{\text{Terminal lactyl units}}{\text{Anhydroglucose units}} = \frac{\text{IA}_b/3}{[\text{IA}_c - \text{IA}_{(a+b)}/3]/7} \quad (2)$$

$$\text{DP}_{\text{PLLA}} = \frac{\text{MS}}{\text{DS}} = \frac{\text{IA}_{(a+b)}/3}{\text{IA}_b/3} = \frac{\text{IA}_a}{\text{IA}_b} + 1 \quad (3)$$

where, molar substitution of the IA_a and IA_b are the resonance peak areas deriving from internal methine protons of lactyls in

PLLA side-chains and terminal methine protons of lactyls in PLLA side-chains, respectively; and the IA_c is the area of all protons of anhydroglucose units.

Hedrick et al.³⁵ reported that DMAP was a highly efficient catalyst for the controlled synthesis of PLLA. Table I showed the research results obtained by using various feed ratios of L-LA/MCC. Based on previous experiments, the polymerization temperature was set at 80°C . It can be seen that the grafting content of PLLA in polymers increased with the increase of weight ratio of LA and DMAP to cellulose. One possible explanation is that L-LA reacted with DMAP to form an intermediate. This intermediate can attack hydroxyl groups of cellulose easier than L-LA. Although there were many PLLA branches on the cellulose chain, with the amount of lactic acid increasing, the gain of each PLLA branch was limited. From Table I, the highest DP value of cellulose-g-PLLA polymer was 3.93. These values were much higher than those reported in the DMAc/LiCl system³⁶ and those in AmimCl with DMAP as a catalyst.³⁷

Crystalline Structure Analysis of Cellulose-g-PLLA

The crystalline structure of PLLA, cellulose, cellulose/PLLA blends, and cellulose-g-PLLA (Figure 3) were examined by WAXD. PLLA showed the strongest diffraction peak at $2\theta = 17^\circ$, whereas cellulose showed the strongest diffraction peak at $2\theta = 22.4^\circ$. However, neither the crystallization peak of PLLA nor those of cellulose were observed on cellulose/PLLA blends and cellulose-g-PLLA polymers. Only a dispersive broad peak around $2\theta = 16.8^\circ$ – 22.4° (20.8° – 22.0° , 16.8° – 19.6°) on cellulose/PLLA blend and $2\theta = 20.6^\circ$ (20.4° , 20.8°) was obtained on cellulose-g-PLLA polymer, which indicates that the cellulose became amorphous after compositing with PLLA. Cellulose-g-PLLA has lower degree of crystallinity which might due to an effect of plasticization caused by covalently linking of PLLA side-chains to the semi-rigid cellulose backbone. Teramoto et al.³⁸ showed that CDA-g-PLLA polymers had a crystalline diffraction pattern, which could be caused by the relatively long PLLA side-chains. The degradation rate would be widely variable not only by altering the copolymer composition but also by controlling the phase structure involving crystalline morphology.

Thermal Properties

Polymer morphology is known to influence degradation and therefore the melting and crystallizing behaviors of graft copolymers were measured by DSC and TGA. Figure 4 shows DSC

Table I. Results and Reaction Conditions of the Cellulose-g-PLLA and Cellulose/PLLA

No.	MCC(g)	AmimCl/MCC (wt/wt)	L-LA (or PLLA) /MCC (wt/wt)	Temp ($^\circ\text{C}$)	-OH/DMAP (mol %)	Reaction time (h)	DP_{PLLA}	MS_{PLLA}
Graft 1	0.6	4%	5/1	90	1.5	9	3.15	4.06
Graft 2	0.6	4%	7/1	90	1.5	9	3.55	4.34
Graft 3	0.6	4%	9/1	90	1.5	9	3.93	4.44
Blend 1	0.6	–	5/1	183	–	0.16	–	–
Blend 2	0.6	–	7/1	183	–	0.16	–	–
Blend 3	0.6	–	9/1	183	–	0.16	–	–

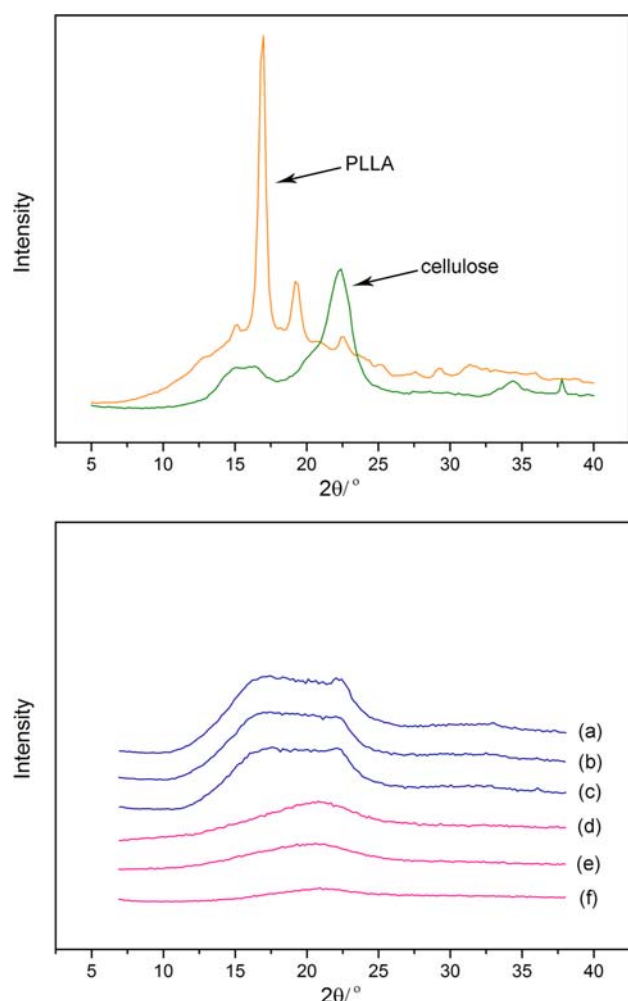


Figure 3. Wide-angle X-ray diffractograms of PLLA, cellulose, and cellulose/PLLA Blend 3 (a), Blend 2 (b), Blend 1 (c), cellulose-g-PLLA Graft 3 (d), Graft 2(e), and Graft 1(f). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

thermograms of cellulose, cellulose/PLLA (Blend 1), cellulose-g-PLLA (Graft 1), and PLLA homopolymer in the second heating scan. In conventional DSC, a reversing event like the glass transition may be hidden by a non-reversing event, such as enthalpic relaxation, so the neat unmodified cellulose did not show a glass transition temperature (T_g) in the standard heating scan. However, using a more sensitive method, Batzer and Kreibich reported a T_g of 230°C for dry cellulose.³⁹ PLLA homopolymer exhibited a T_g at 60.6°C. A T_g of 59.1°C and 40.3°C were observed for cellulose blend and cellulose-g-PLLA polymer, respectively. This may have resulted from the expansion of intermolecular distance and the enhancement of chain mobility due to the introduction of PLLA.⁴⁰ Compared to the unmodified cellulose, the decrease in T_g for cellulose/PLLA blend and cellulose-g-PLLA polymer suggested the PLLA played an effective role as “internal” plasticizer to the originally semirigid cellulose material. It should be noted here that no melting peak was observed by DSC for the polymer products, suggesting that the synthesized cellulose-g-PLLA polymers were amorphous. This conclusion is in accordance with that obtained by WAXD measurement.

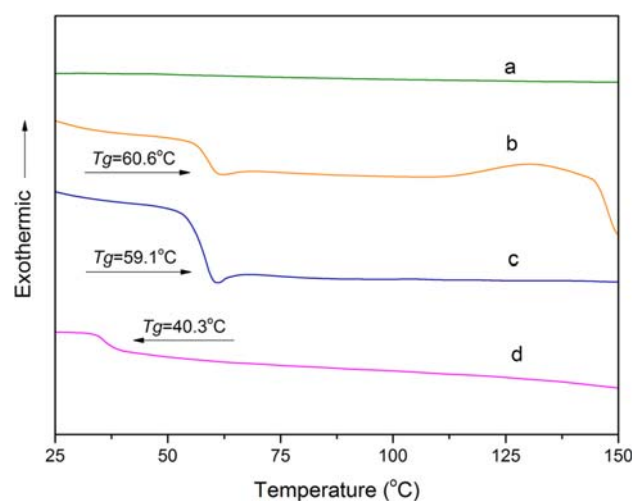


Figure 4. DSC thermograms of (a) cellulose, (b) PLLA, (c) cellulose/PLLA Blend 1, and (d) cellulose-g-PLLA Graft 1. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The thermal stability of blend and graft polymer was evaluated by TGA and the data given in Table II and shown in Figure 5. The initial thermal decompositions of cellulose and PLLA homopolymer took place at 312 and 348°C, respectively. Whereas the cellulose/PLLA blend and cellulose-g-PLLA polymer exhibited their initial thermal decomposition at 342 and 237°C, respectively. The decreased thermal stability of the graft polymer should be attributed to the introduction of PLLA into the cellulose, which destroyed the crystalline structure of cellulose to some extent. However, the decreased thermal stability of the graft polymer decreased indistinctly. This was also confirmed by WAXD and DSC results.

Hydration Properties

The cellulose/PLLA blends and cellulose-g-PLLA polymers degraded via hydrolytic processes of the ester chains of PLLA. Water accessibility to these bonds would determine the rate of degradation.^{41,42} Accordingly, the rates for the degradation may depend on the hydrophilicity and crystallinity of the blend and graft polymer. Cellulose is relatively hydrophilic, but with a semi-crystalline structure. Figure 6 showed the degree of hydration of polymers prepared from differing amounts of PLLA. The water uptake capability of cellulose/PLLA blends had improved a little but not obviously. All the cellulose-g-PLLA showed high water uptake capabilities; and the water content

Table II. Thermal Properties of Cellulose/PLLA Blend and Cellulose-g-PLLA Polymer

Sample	T_g	T_{onset}	T_{max}
Cellulose	–	312	346
PLLA	60.6	348	381
Blend 1	59.1	342	379
Graft 1	40.3	237	282

T_{onset} : onset decomposition temperature; T_{max} : maximum decomposition temperature.

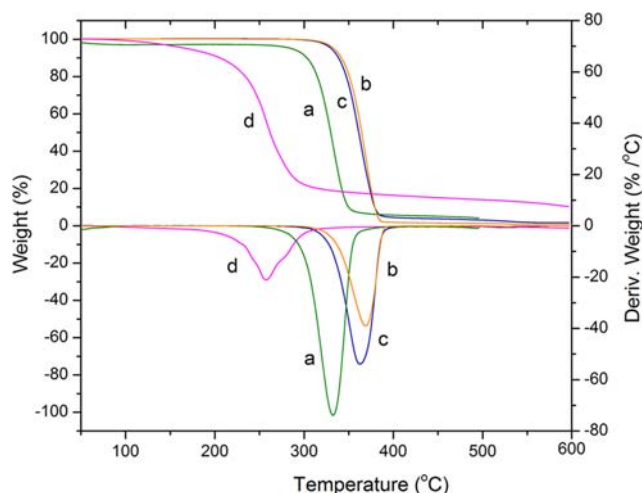


Figure 5. TG and DTG thermograms of (a) cellulose, (b) PLLA, (c) cellulose/PLLA Blend 1, and (d) cellulose-g-PLLA Graft 1. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

increased with the increase in the amounts of DP_{PLLA} which may be due to the increase of the degree of network structures, but the rate of water uptake decreased with the increase in the amounts of DP_{PLLA} which may be due to the denser network structures.

Hydrolyzed by Alkali

The weight losses of the samples in alkali liquor were shown in Figure 7(a). Both PLLA and cellulose could be degraded in alkali liquor. And PLLA was more stable in alkali than cellulose. Degradation reaction of cellulose in alkaline could create new reducing end base and decrease the degree of polymerization and fiber strength.

For cellulose/PLLA blends and cellulose-g-PLLA, the weight loss decreased with the increase of the amount of PLLA in the polymer which might due to polyester-like macromolecule rapidly decaying. But different crystalline structures had different degradation rates. Solid PLLA and microcrystalline cellulose were

both partially crystalline polymers, whose crystalline region was packed very compactly, so they possess less degradability. However, after blending and graft polymerization, cellulose/PLLA blends, and cellulose-g-PLLA exhibited lower crystallinity. Lower crystallinity, which could easily stimulate the biological and chemical reagents, was conducive to the degradation of materials. So, cellulose/PLLA blends and cellulose-g-PLLA had good degradability, and the cellulose-g-PLLA possess better degradability than cellulose/PLLA blends. These results were in accordance well with the WAXD results.

Cellulose-g-PLLA was investigated farther because of its better degradability. Figure 7(b) shows that the weight loss of cellulose-g-PLLA in alkali liquor changes depending on time and DP_{PLLA} of the graft polymers. Through data fitting a formula of weight loss was obtained ($r^2 = 0.9908$):

$$W_{\text{loss}} = 18.54 \times t - 565.89 \times D - 0.45 \times t^2 + 73.32 \times D^2 - 2.56 \times t \times D + 1093.98$$

where, r^2 is the coefficient of determination. W_{loss} is the weight loss of cellulose-g-PLLA at time t . D represents the DP_{PLLA} of the graft polymer.

Biodegradation Studies

PBS hydrolysis. Hydrolysis had great effects on biodegradation of polymers in enzyme solution, therefore the hydrolysis of polymers should be researched first. Figure 8(a) showed that the weight loss decreased with the increase of the amount of PLLA in the polymer. These results were in accordance well with those of hydrolyzed in alkali. Hydrolysis of PLLA was the main reaction of cellulose-g-PLLA in PBS. The good water affinity of cellulose allowed water penetrating into the polymer molecules and breaking ester bond inside, leaving low molecular mass polymers. Moreover, the hydrolysis process can be promoted by the increase of the concentration of terminal carboxyl group, with which PLLA was finally resolved into carboxylic acid and alcohol.

The PBS solution entered into the amorphous regions and the crystalline regions in sequence. The hydrolytic proceeded more

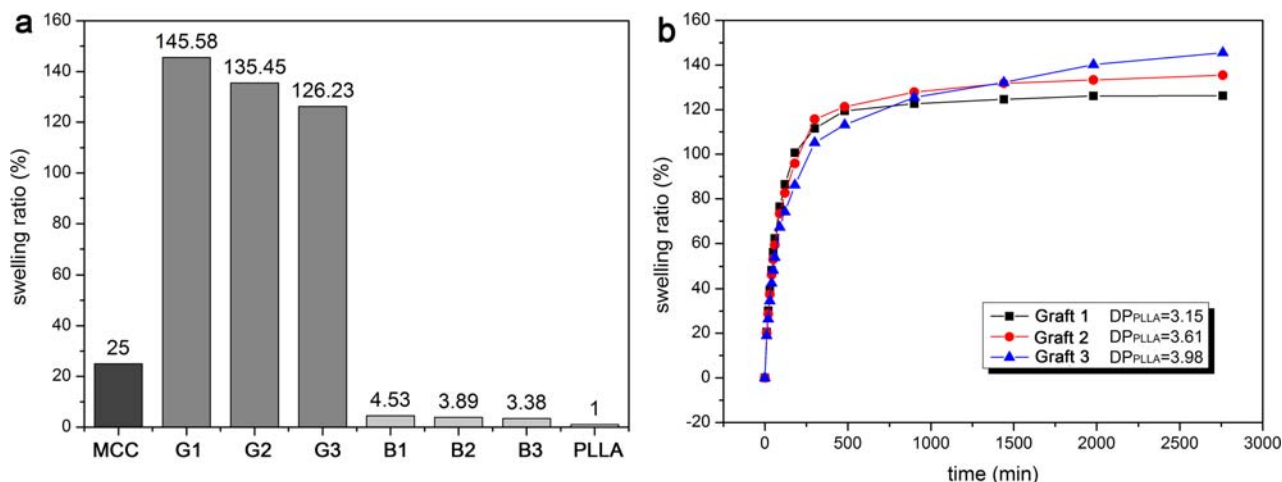


Figure 6. Degree of hydration of cellulose/PLLA blends and cellulose-g-PLLA. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

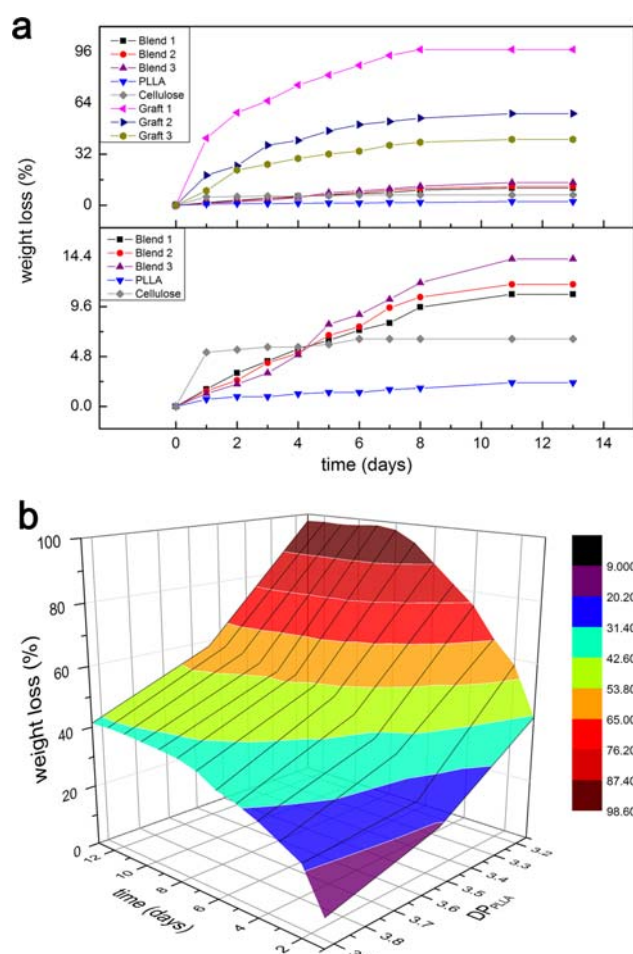


Figure 7. Degradability of cellulose/PLLA blends and cellulose-g-PLLA in alkali liquor. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

preferentially in amorphous regions than in crystalline regions. Biodegradation process of PLLA was also indirect.⁴³ First, PLLA was hydrolyzed by cutting the unstable bonds and hydrolysing into oligomers. Second, it could be further degraded by enzymes into lactic acid. So the performance of polymer biodegradation was greatly affected by its hydrolysis ability.

Figure 8(b) shows that the weight loss of cellulose-g-PLLA in PBS changes depending on time and DP_{PLLA} of the graft polymers. Through data fitting a formula of weight loss was obtained ($r^2 = 0.9683$):

$$W_{\text{loss}} = 27.25 \times t + 374.77 \times D - 0.36 \times t^2 - 54.76 \times D^2 - 5.55 \times t \times D - 625.08$$

where, r^2 is the coefficient of determination. W_{loss} is the weight loss of cellulose-g-PLLA at time t . D represents the DP_{PLLA} of the graft polymer.

Enzymatic Hydrolysis. Cellulose-g-PLLA was hydrolyzed by lipase to produce lactic acid, which can produce strong absorption in 210 nm wavelength. UV absorption represented the dissolved amount of aqueous lactic acid in a solution; that was, PLLA materials in enzyme solution were degraded to lactic acid,

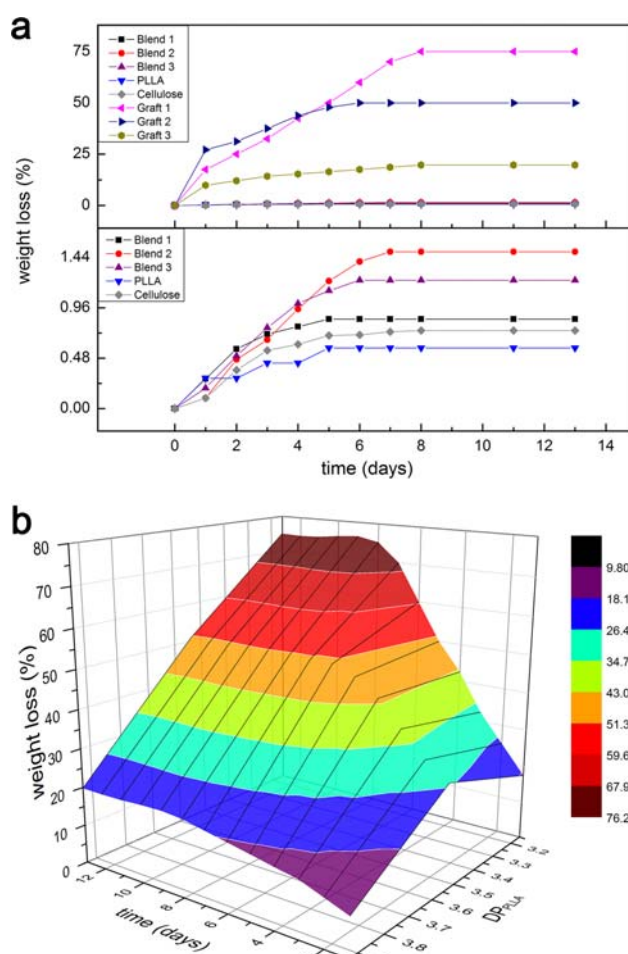


Figure 8. Degradability of cellulose/PLLA blends and cellulose-g-PLLA in PBS. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

and the concentration of it, was quantified by the analysis of UV absorption. Figure 9(a) showed that the weight losses of Graft 3, 2, 1 and Blend 3, 2, 1 finally decreasing in sequence. Meanwhile, it could be also found that the weight loss increased by the extension of the processing of the lipase, but 3 days later weight loss rose more slowly towards a balance. These results strongly proved that this polymer could be hydrolyzed by lipase and when the ester bonds were hydrolyzed to certain degree, even if the lipase processing time was extended, the reaction in the fluid of lactic acid would not be more dramatic and the weight loss curve tended towards balance.

The correlation was examined between actual degradability data and properties of samples those were presumed to affect degradability. Based on the results from correlation analysis, the amount of PLLA in the polymer appeared to be the most influential factor for the degradability. Crystallinity was exhibited to be negatively correlated. And, in enzyme solution, alkaline liquor, and PBS system, the degradation rate of the polymer decreased in above sequence. The cellulose/PLLA blend and cellulose-g-PLLA polymer were hydrolyzed first and then further degraded by enzymes.

Figure 9(b) shows that the weight loss of cellulose-g-PLLA in enzyme solution changes depending on time and DP_{PLLA} of the

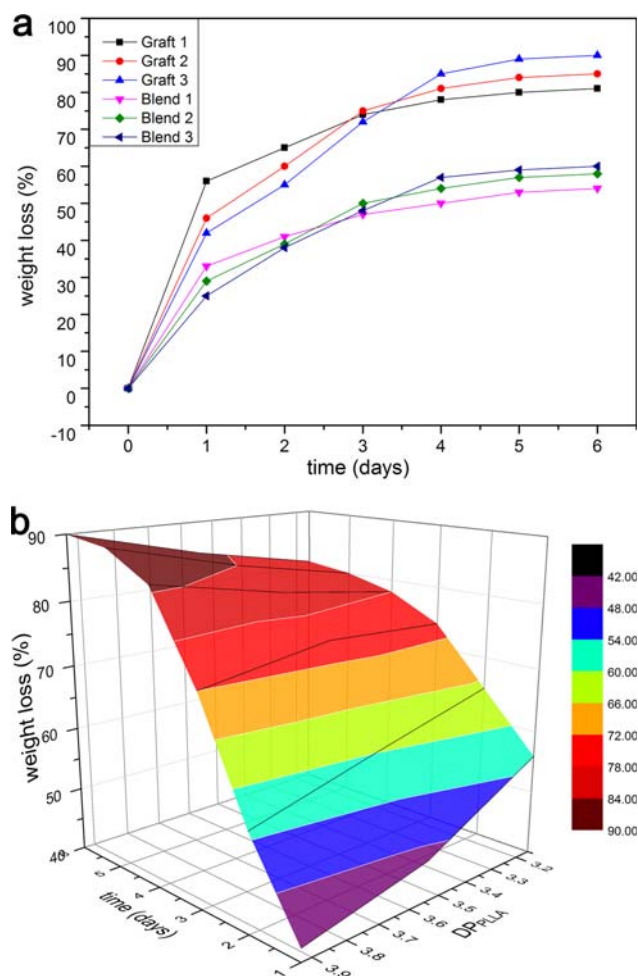


Figure 9. Degradability of cellulose/PLLA blends and cellulose-g-PLLA in enzyme solution. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

graft polymers. Through data fitting a formula of weight loss was obtained ($r^2 = 0.9877$):

$$W_{\text{loss}} = -3.67 \times t - 42.74 \times D - 1.74 \times t^2 + 2.73 \times D^2 + 6.63 \times t \times D + 146.02$$

where, r^2 is the coefficient of determination. W_{loss} is the weight loss of cellulose-g-PLLA at time t . D represents the DP_{PLLA} of the graft polymer. The formula of weight loss could guide the modification of cellulose-g-PLLA materials and make degradability of this material controllable.

CONCLUSIONS

This study presented here demonstrated that the blends and graft polymers based on the cellulose and PLLA could be prepared successfully to develop the novel degradable materials. The cellulose-g-PLLA polymer was synthesized via ring-opening polymerization (ROP) by using DMAP as an organic catalyst in an ionic liquid AmimCl. The blending method and graft polymerization was shown to influence polymer crystallization and promote polymer degradability. Cellulose-g-PLLA was shown to have good and controllable degradability. Therefore, the

material was expected to be environmentally friendly. In the near future, such graft material might be ideal platforms for the design of carrier biomaterials in the field of controlled release of drugs and regenerative medicine.

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