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Poly(L-lactide)/starch blends compatibilized with poly(L-lactide)-*g*-starch copolymer

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Abstract

The poly(L-lactide) (PLLA)/starch blends were prepared by the PLLA grafting starch (PLLA-*g*-St) copolymers as a compatibilizer, and their thermal, mechanical and morphological characterizations were performed to show the better performance of these blends compared to the virgin PLLA/starch blend without the compatibilizer, including PLLA crystallinity, interfacial adhesion between the PLLA matrix and starch dispersive phases, mechanical test, medium resistance, and contact angle. The 50/50 composite of PLLA/starch compatibilized by 10% PLLA-*g*-St gave a tensile strength of 24.7 MPa and an elongation at break of 8.7%, respectively, vs. 11.3 MPa and 1.5%, respectively, for the simple 50/50 blend of PLLA/starch.

Keywords: PLLA-*g*-starch; PLLA/starch; Compatibilizer; Blend; Interfacial adhesion

1. Introduction

The environmental pollution caused by the disposal of non-degradable plastic wastes attracts more attention to the research and development on the biodegradable polymers. However, up to the present the biodegradable polymers cannot be used for wide applications because of their limitations on prices or mechanical and physical properties. Starch is a potentially useful material for biodegradable plastics because of its natural abundance and low cost. However, the starch-based materials, such as the thermoplastic starch, produced by conventional melt-processing usually exhibit very poor mechanical properties, mainly due to the thermal decomposition of starch before melting, the strong water absorption and the poor interfacial adhesion with other components. In order to solve these problems, various physical or chemical modifications of the starch granules have been considered, including blending (Dubois, Krishnan, & Narayan, 1999; Koenig & Huang, 1995; Kweon, Cha, Park, & Lim, 2000; Kweon & Lim, 2001; Lee, Lee, & Hong, 1997; Stenhouse et al., 1993; Vaidyia & Bhattcharya, 1994) and chemical modifications (Athawale & Lele, 2000; Cho & Lee, 2002; Choi, Kim, & Park, 1999a, b; Chen, Ni, Bian, Chen, & Jing, 2005; Fanta, Felker, & Shogren, 2004; Krishnan et al., 1996; Narayan, Krishan, & Dubois, 1996, 1997; Rutot, Degee, Narayan, & Dubois, 2000; Zhai, Yoshii, Tamikazu & Kamaruddin, 2002).

Many researchers have studied biodegradable polymer blends containing starch as one component. Since Griffin prepared starch-filled plastics, several kinds of starch/synthetic polymer blends have been developed. Because the other component is usually non-biodegradable, these blends could not be used as biodegradable plastics. In order to prepare completely biodegradable composites, starch is blended with aliphatic polyesters such as poly-ε-caprolactone (PCL) (Delben et al., 2004; Koenig & Huang, 1995). With increasing starch content, the mechanical properties of the PCL/starch blends generally become poorer. This can be considered as the incompatibility between the hydrophobic PCL and the hydrophilic surface of starch. Choi et al. (1999a, b) used

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starch-*g*-PCL as a compatibilizer to enhance the interfacial adhesion between PCL and starch phases, the properties of the blend were improved obviously. Avella, Errico, Laurienzo, & Rimedio (2000) prepared PCL/high amylose starch blends in which the low molecular weight PCL modified by reacting its terminal groups with pyromellitic anhydride was used as a compatibilizer. Sun (Zhang & Sun, 2004) prepared PLA/starch blends compatibilized by maleic anhydride, the interfacial adhesion between PLA and starch was significantly improved, and thus, remarkable increase in mechanical properties was observed.

In this study, we use PLLA grafting starch (PLLA-*g*-St) as a novel compatibilizer to prepare PLLA/starch blends and investigate the compatibilizing effect of PLLA-*g*-St on the mechanical and physical properties of the PLLA/starch blends.

2. Experimental section

2.1. Materials

The corn starch was from Changchun Dacheng Corn Development Co. Ltd in Jilin province, China. The water content in the starch was about 12% in weight measured by water loss at 60 °C in a vacuum oven. The PLLA was synthesized in our laboratory and its molecular weights measured with GPC were $M_n=98{,}000$ and $M_w=117{,}000$.

The compatibilizer, PLLA-grafted-starch (PLLA-*g*-St), was synthesized and characterized as described in our previous study (Chen, Qiu, Chen, & Jing, 2005): the starch surfaces were firstly modified by reacting the hydroxyl groups on the starch with L-lactic acid, and then the PLLA-*g*-St was synthesized in situ by the ring-opening graft polymerization of L-lactide (LLA) monomers onto the modified surfaces of the starch granules in the presence of $Sn(Oct)_2$ as a catalyst depicted in Scheme 1. After the polymerization reaction, the unreacted LLA monomers and PLLA homopolymer were washed off with ethanol and toluene, respectively. The grafting rate and the thermal properties of the final product, PLLA-*g*-St, were summarized in Table 1.

2.2. PLLA/starch blend preparation

The PLLA/starch blends with various PLLA-*g*-St contents as shown in Table 2 were prepared by mixing in an internal mixer (Haake) at 150 °C for 15 min. The PLLA, starch and the compatibilizer PLLA-*g*-St were added simultaneously in the mixer. Then the mixture was molded into 2–3 mm thick sheets by hot-pressing at 130 °C. The dumbbell-shaped specimens for tensile measurements were cut from the sheets in accordance to ASTM Standard D638 V.

2.3. Differential scanning calorimetry (DSC) measurements

The crystallinities of PLLA component in the blend were evaluated using DSC. The DSC analysis was performed at a heating rate of 10 °C/min under N_2 atmosphere on a Perkin Elmer Pyris 1 instrument. The crystallization degree and melting point of the composites were measured by DSC. Crystallinity of the PLLA in the composites was calculated from the following formula (Huang et al., 1998)

$$\text{Crystallity (\%)} = \Delta H_M/93.7 \times 100$$

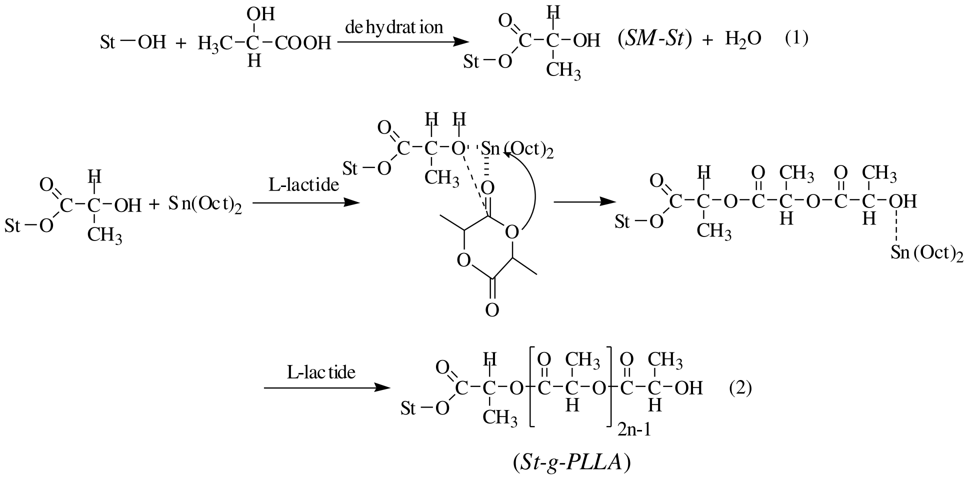
where ΔH_M is the melting enthalpy (in J/g) calculated from the fusion peak of DSC (the second heating run). And the value 93.7 (J/g) is the theoretical enthalpy of completely crystalline PLLA.

2.4. Mechanical properties

The mechanical properties were measured at room temperature on an Instron 1121 tester at a constant deformation rate of 10 mm/min. A minimum of three specimens was tested and the results were averaged. The typical stress–strain curves of the PCL/starch blend were given in Fig. 2.

2.5. SEM observation

The morphology of the PLLA/starch was investigated by a Model XL 30 ESEM FEG from Micro FEI Philips after sputter



Scheme 1. The surface modification reaction of starch with L-lactic acid (1) and the $Sn(oct)_2$ initiated polymerization mechanism of L-LA with the modified starch (2).

Table 1
The grafting rate and the thermal properties of PLLA-*g*-St compared to the pure PLLA

Sample	Grafting rate (%)[a]	T_m (°C)	ΔH_m (J/g)	X_c (%)[b]
PLLA$_9$-*g*-St	9	–	–	–
PLLA$_{36}$-*g*-St	36	124.5	9.2	9.8
PLLA$_{64}$-*g*-St	64	136.0	15.6	16.6
PLLA (M_n=98,000)	–	154.1	45.2	48.2

[a] According to Chen et al. (2005).

[b] X_c is calculated by only considering the weight of PLLA grafts. According to Huang et al. (1998).

coating of gold on the fractured surface of the dumbbell specimens.

2.6. Contact angle measurements

Contact angle measurements were performed with a Kruss DSA10 MK2 (Germany) apparatus. A water droplet was dropped on the surface of a small sample cut from a dumbbell specimen. The evolution of the droplet shape was recorded by a CCD video camera and was analyzed to determine the contact angle evolution.

2.7. Medium resistance measurements

The medium-resistance measurement of the blends to 0.5 mol/L acid solution, 0.5 mol/L alkaline solutions and pure water was performed by dispersing the blend films in the corresponding aqueous solutions at room temperature for 24 h, and measuring the weight loss of the films.

3. Results and discussion

3.1. Thermal analysis of the composites

The PLLA grafting rate and thermal properties of PLLA-*g*-St compatibilizers are summarized in Table 1. The grafting rate is defined as the weight content of the grafted PLLA in the graft copolymer and was determined by Chen, Qiu, Chen, Jing (2005). As shown in Table 1, the grafting rate can be changed in a wide range by adjusting the grafting conditions such as feed composition, catalyst concentration, etc. The T_m, ΔH_m and X_c of the PLLA-*g*-St determined by DSC are closely dependent on the grafting rate. Sample 1 has a grafting rate of 9%, and is not crystalline at all. The other two are crystalline and show increasing T_m, ΔH_m and X_c with the grafting rate. This is because the length of the PLLA chains grafted on the starch surfaces increases with the grafting rate and the crystallization behaviors of the PLLA chains are dependent on their length. Nevertheless, the crystal structure of the grafted PLLA is much less perfect than that of the PLLA homopolymer, as indicated by the T_m and ΔH_m data in Table 1, because of the limited graft length of PLLA.

Table 2
PLLA/starch blends compatibilized by PLLA-*g*-St and their thermal analysis data

Sample entry	Compatibilizer[a]		T_m (°C)	ΔH_m (J/g)	X_c (%)[b]
	Polymer	Content (wt%)			
1	PLLA$_9$-*g*-St	10	137.6	10.4	11.0
2	PLLA$_{36}$-*g*-St	10	139.2	19.5	20.9
3	PLLA$_{64}$-*g*-St	2	136.1	9.3	9.9
4	PLLA$_{64}$-*g*-St	5	137.4	17.0	18.1
5	PLLA$_{64}$-*g*-St	10	140.5	20.4	21.7
6	PLLA$_{64}$-*g*-St	20	139.6	19.7	21.0
PLLA/starch	None		134.0	7.2	7.8

[a] The weight ratio of PLLA and starch is 50:50 for all blend samples. PLLA-*g*-starches in Table 1 were used as compatibilizers. Their content is with respect to the total weight of PLLA and starch.

[b] X_c is calculated by considering all PLLAs in both PLLA component and PLLA-*g*-starch compatibilizer.

Fig. 1 shows the typical DSC curves of PLLA (a), PLLA$_{64}$-*g*-St (b), simple PLLA/starch (1:1) blend (c) and PLLA$_{64}$-*g*-St-compatibilized PLLA/starch (1:1) blend (d). The PLLA (M_n= 98,000) shows a T_m at 154 °C; the PLLA$_{64}$-*g*-St gives a T_m at 141 °C; the simple PLLA/starch blend shows a broad and weak melting transition over 120–140 °C; and the PLLA$_{64}$-*g*-St-compatibilized blend gives a sharp endothermic peak at 140 °C, being higher than those of the PLLA$_{64}$-*g*-St and the simple PLLA/starch blend. This difference may be ascribed to the contribution of the PLLA-*grafted*-starch compatibilizer.

It is well known that the simple PLLA/starch blends usually show very poor mechanical properties because of the severe phase separation between the two components PLLA and starch and the weak interactions between the two phases. Adsorption of water in the starch phase is another reason for the poor properties of the blends. In order to enhance the interphase interactions, PLLA grafted starch is used as a compatibilizer in the PLLA/starch blends. It is expected that its PLLA grafts can mix and co-crystallize with the PLLA components, its starch part can join the starch phase, and therefore, the PLLA grafted starch will play a role of tying molecules between the PLLA phase and starch phase. Obviously, structure and content of the

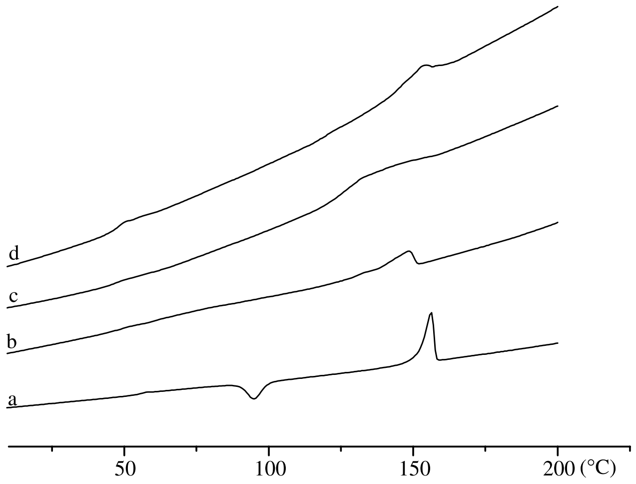


Fig. 1. The DSC curves (second heating run) of: (a) PLLA; (b) PLLA$_{64}$-*g*-St; (c) simple PLLA/starch blend and (d) sample entry 5 in Table 2.

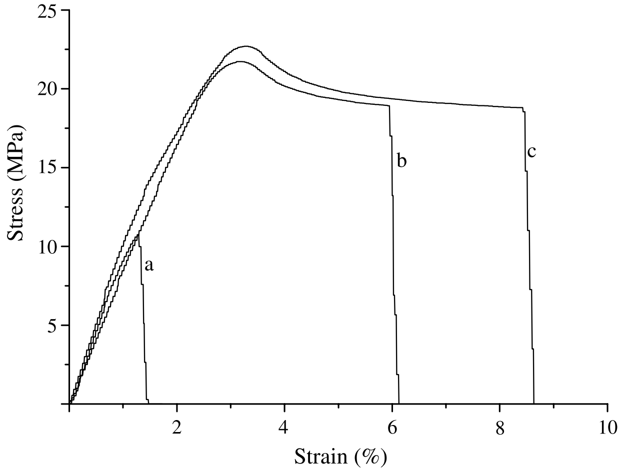


Fig. 2. Typical stress–strain curves of PLLA/starch blends: (a) simple PLLA/starch (1:1) blend; (b) sample entry 4 in Table 2; (c) sample entry 5 in Table 2.

PLLA grafted starch will determine the final structure and performance of the blends. As shown in Table 2, all compatibilized blends exhibit higher T_ms and X_cs than the simple PLLA/starch blend. Among them, samples 1, 2 and 5 contain the same amount of compatibilizers, but the compatibilizers have different grafting rates, from 9 to 64%, correspondingly, the T_m and X_c increase with the grafting rate. Samples 3–6 contain the same compatibilizer but its content changes from 2 to 20%. Consequently, sample 5 displays the maximum T_m and X_c, indicating that further increase of the compatibilizer is no use.

3.2. Mechanical properties and SEM analysis

Mechanical properties such as tensile modulus (E), yield strength (σ_y), strength at break (σ_b) and elongation at break (ε_b) were evaluated from the stress–strain curves. Typical stress–strain curves of PLLA/starch blends compatibilized with various PLLA-*g*-St copolymers are shown in Fig. 2 and the related data are summarized in Table 3. As expected, addition of starch fillers into PLLA matrix leads to significant reduction of the mechanical properties due to the poor filler/matrix interfacial adhesion. When the compatibilizer is incorporated into the blends, the mechanical properties are substantially improved. With the PLLA-*g*-St content increasing from 2 to 10%, E, σ_y σ_b, and ε_b all increase, but when the PLLA-*g*-St content increases to 20%, these values all decrease. This is in agreement with the dependence of T_m and X_c on the PLLA-*g*-St content discussed in Section 3.1. That is to say, the PLLA grafted starch really plays a role of compatibilizer because it is incorporated into both the PLLA phase and the starch phase. It does not only promote a better dispersion of the starch granules in the PLLA matrix, but also reinforces the adhesion between the fillers and the matrix. Because the PLLA grafted starch itself is a polymer, its compatibilizing effect is more significant than other small molecular compatibilizers[23]. Moreover, the compatibilizer PLLA-*g*-St is cheap and biodegradable, its wide industrial applications are expected.

Table 3
Tensile properties of PLLA/starch blend compositions and PLLA

Sample entry[a]	σ_b (MPa)	ε_b (%)	E (GPa)	σ_y (MPa)
1	18.9	4.1	0.76	18.6
2	19.6	5.6	0.80	19.8
3	16.4	2.8	0.69	16.9
4	22.9	5.9	0.73	22.9
5	24.7	8.7	0.85	24.7
6	19.6	7.2	0.84	19.9
PLLA/starch	11.3	1.5	0.67	–
PLLA	55.4	12.3	3.00	50.9

σ_b, strength at break; ε_b, elongation at break; E, tensile modulus; σ_y, strength at yielding.

[a] Sample entry 1–6 is referred to Table 2.

A morphological analysis was also performed on the fractured surface of the sample after the tensile test. The SEM micrographs of the PLLA/starch blends with different contents of compatibilizer are shown in Fig. 3a–d, respectively. The simple PLLA/starch blend shows a poor interfacial adhesion (Fig. 3a and c). A clear edge and aperture between the starch granules and PLLA matrix are observed. On the contrary, it is observed that the starch grains are better distributed and covered by PLLA material in the samples containing the PLLA-*g*-St compatibilizer (Fig. 3b and d), confirming a good interconnection between the starch granules and PLLA matrix. The edge and the interphase between the two phases become more blurry with the increasing content of PLLA-*g*-St.

3.3. Contact angle measurements

The contact angle formed between a water droplet placed at the surface of a material and the kinetics of spreading is related to the hydrophilic character of the material. The initial angle (in degree) and the kinetic of water sorption on the surface are given by this method. The blend material behaviors are quantitatively illustrated by the initial contact angle just after

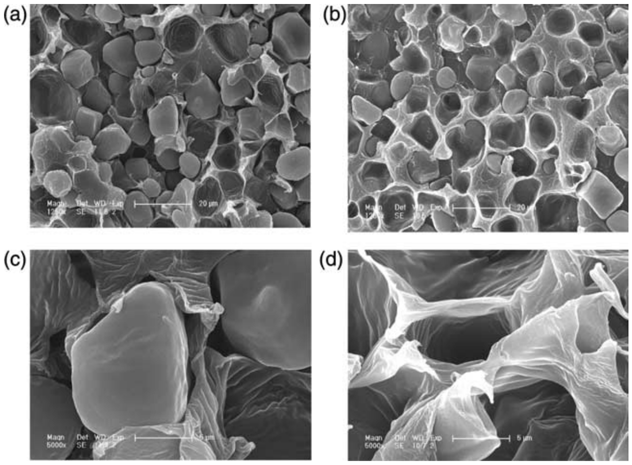


Fig. 3. SEM micrographs of the PLLA/starch blends: (a) simple PLLA/starch (1:1) blend; (b) PLLA/starch/2% St-*g*-PLLA (sample entry 3 in Table 2); (c) the magnified image of PLLA/starch (1:1) blend; (d) the magnified image of sample entry 3.

Table 4
Contact angle measurements of PLLA/starch blends and PLLA

Sample entry[a]	Initial value (deg.)[b]	Slope at the origin (°/s)
1	72	−0.1
2	83	−0.1
3	69	−0.25
4	79	−0.2
5	85	−0.1
6	84	−0.1
PLLA/starch	52	−1.5
PLLA	97	−0.05

[a] Sample entries 1–6 are referred to Table 2.

[b] The data were collected by mean of five independent experiments.

deposition of a droplet and by the evolution rate of the contact angle with time. The results of the contact angle measurements are presented in Table 4. For the pure PLLA, the contact angle is 97° due to its hydrophobic nature. With the addition of the hydrophilic starch, the contact angle of the PLLA/starch blend decreases to 52°. When PLLA-St compatibilizer is added to the blend, the value of the contact angle increases and this increase is dependent on both PLLA-St content and composition as shown in Table 4. For the simple PLLA/starch blend without the PLLA-*g*-St compatibilizer, the evolution rate of the water contact angle is more rapid than that with PLLA-*g*-St, because of the hydrophilic nature of the starch. When the PLLA-*g*-St is incorporated into the blends, the evolution of contact angle with time became slower. In all cases, the presence of PLLA-*g*-St leads to a significant improvement of the material hydrophobicity. These behaviors provide further evidence for the improved compatibility or the reinforced adhesion between the starch granules and the PLLA matrix in the PLLA-*g*-St compatibilized system. Because of the presence of the PLLA-*g*-St compatibilizer, the hydrophilic starch granules appear to be hidden in the hydrophobic PLLA matrix.

3.4. Medium-resistance

It is well known that water resistance is a very important factor for practical applications of starch-based materials, because starch is usually poor in storage stability due to its sensitivity to moisture. The medium-resistances of the PLLA/starch blends with or without PLLA-*g*-St to 0.5 mol/L acid solution, 0.5 mol/L alkaline solution and pure water are measured at room temperature for 24 h, respectively. Dispersed in water or an acid solution, the films always gain a certain weights, while in an alkaline solution they loses weights at the beginning stage. The weight increase is due to the water adsorption by the starch in the blend and the weight-loss is due to the degradation of the starch catalyzed by the alkali. As shown in Table 5, the stabilities in all three media of the compatibilized blends are improved compared to the simple PLLA/starch (50/50) blend. Among them the blend with 10% of PLLA_{64}-*g*-St is the best. Owing to the improved medium-resistance, the blend is expected to find industrial use because it does not become swollen or sticky when contacted with water or moisture.

Table 5
The medium-resistance of the PLLA/starch blends

Sample entry[a]	Weight change (wt%)		
	In 0.5 mol/L HCl	In 0.5 mol/L NaOH	In H_2O
1	+2.8	−15.8	+2.3
2	+2.3	−12.3	+1.8
3	+4.6	−19.7	+4.2
4	+3.6	−16.8	+2.4
5	+2.1	−10.9	+1.3
6	+2.3	−11.3	+1.2
PLLA/Starch	+19.5	−37.3	+19.5

[a] Sample entries 1–6 are referred to Table 2.

4. Conclusion

The use of PLLA-*g*-St as a compatibilizer in PLLA/starch blends can improve the performances without changing their whole biodegradability. PLLA-*g*-St is a good compatibilizer for the blend of hydrophobic PLLA and hydrophilic granular corn starch. The PLLA-*g*-St proves effective to improve the interfacial adhesion and the mechanical properties of the composites. These environmental compatible materials are characterized by less cost than the neat PLLA and display all required qualities of a disposable plastic. Moreover, the amount of PLLA-*g*-St compatibilizer can be selected to tailor the properties of the composites for specific applications. The PLLA-*g*-St compatibilized PLLA/Starch blends show better mechanical properties and stronger medium-resistance in comparison with the simple starch/PLLA blend. Therefore, they can be one of the good candidates in the potential application as disposal plastic or fertilizer delivery carrier.

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