Compatibilizing Effect of Starch-*grafted*-Poly(L-lactide) on the Poly(ε-caprolactone)/Starch Composites

Li Chen,[1] Zhe Zhang,[1] Xiuli Zhuang,[2] Xuesi Chen,[2] Xiabin Jing[2]

[1]Department of Chemistry, Northeast Normal University, Changchun 130022, People's Republic of China
[2]State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Changchun 130022, People's Republic of China

ABSTRACT: The poly(ε-caprolactone) (PCL)/starch blends were prepared with a coextruder by using the starch *grafted* PLLA copolymer (St-*g*-PLLA) as compatibilizers. The thermal, mechanical, thermo-mechanical, and morphological characterizations were performed to show the better performance of these blends compared with the virgin PCL/starch blend without the compatibilizer. Interfacial adhesion between PCL matrix and starch dispersion phases dominated by the compatibilizing effects of the St-*g*-PLLA copolymers was significantly improved. Mechanical and other physical properties were correlated with the compatibilizing effect of the St-*g*-PLLA copolymer. With the addition of starch acted as rigid filler, the Young's modulus of the PCL/starch blends with or without compatibilizer all increased, and the strength and elongation were decreased compared with pure PCL. Whereas when St-*g*-PLLA added into the blend, starch and PCL, the properties of the blends were improved markedly. The 50/50 composite of PCL/starch compatibilized by 10% St-*g*-PLLA gave a tensile strength of 16.6 MPa and Young's modulus of 996 MPa, respectively, vs. 8.0 MPa and 597 MPa, respectively, for the simple 50/50 blend of PCL/starch. At the same time, the storage modulus of compatibilized blends improved to 2940 MPa. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 117: 2724–2731, 2010

Key words: PCL/starch blend; Starch-*g*-PLLA; compatibilizer; interfacial adhesion

INTRODUCTION

In the last decades, biodegradable polymers and blends have been considered as an ultimate solution to the public environmental problem caused by the disposal of traditional nondegradable petroleum-based polymers.[1,2] However, up to now the biodegradable polymers cannot be used for wide applications because of their limitations on prices or mechanical and physical properties. Starch, a nature biodegradable polymer from renewable resources, is a potentially useful material for biodegradable plastics because of its natural abundance and low cost. But starch itself is not suitable for practical applications because of the brittleness increasing with time and the strong water absorption. The starch-based materials produced by conventional melt-processing, such as the thermoplastic starch, usually exhibit very poor mechanical properties, mainly because of the thermal decomposition of starch before melting, the strong water absorption, and the poor interfacial adhesion with other components. To solve these problems, various physical or chemical modifications of the starch granules have been considered, including blending[3–9] and chemical modifications.[10–19]

To obtain completely biodegradable materials with satisfactory mechanical properties, starch is blended with biodegradable aliphatic polyesters such as poly(L-lactide) and poly(ε-caprolactone) (PCL). The blend of starch/PCL is one of the well studied biodegradable polymer blends, as both materials are commercially available and widely produced.[3,20–23] Koening and Huang[3] studied the blends of high-amylose and waxy starch granules with PCL. The blends were found to be mechanically compatible but phase separated. Averous et al.[20] reported the blend of wheat thermoplastic starch with PCL. Addition of PCL to a thermoplastic starch matrix overcomes some weaknesses of pure thermoplastic starch, such as moisture sensitivity and size stability. Thermal and hydrophobicity studies have shown a fairly low compatibility between these two polymers. Hydrophobic aliphatic polyesters and hydrophilic starches are thermodynamically immiscible, which leads to poor adhesion between the two components, and

show poor and irreproducible performance. Various compatibilizers and additives have been evaluated to improve the interface between starch and the biodegradable polyesters.[24–26] It is confirmed that poly(ethylene glycol) (PEG) with proper molecular weight is the most commonly used compatibilizer and the most investigated for starch-based blends.[27] PEG could stabilize the PCL/starch blends by locating at the interface and interact with both PCL phase and starch phase. Choi et al.[28] and Bhattacharya and coworkers[29] used 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[30] 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. Noomhorm and Tokiwa[31] studied the influence of poly(dioxolane) (PDXL), a poly(ethylene oxide-alt-methylene oxide), as compatibilizer on poly (ε-caprolactone) (PCL)/tapioca starch (TS) blends. The molecular weight effect of PDXL on the PCL/TS blends showed that mechanical properties of PCL/TS/PDXL blends from low molecular weight (M_n = 10,000) and high molecular weight (M_n = 200,000) PDXL were rather dependent on TS content.

Our group has prepared the amphiphilic starch-*g*-poly(L-lacide) (St-*g*-PLLA),[32] which has a core-shell structure with a hydrophilic core of starch and a shell hydrophobic of PLLA grafts. Previous research conducted in our laboratory indicated that the St-*g*-PLLA can be used as a compatibilizer in PLLA/starch blends, which can improve the performances without changing their whole biodegradability.[33] The St-*g*-PLLA proved effective to improve the interfacial adhesion and the mechanical properties of the composites. In this study, we use St-*g*-PLLA as a compatibilizer to prepare PCL/starch blends and to investigate the compatibilizing effect of St-*g*-PLLA on the mechanical and physical properties of the starch/ St-*g*-PLLA/PCL blends.

EXPERIMENTAL

Materials

The corn starch was from Changchun Dacheng Corn Development 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. Two PCL samples were synthesized in our laboratory, and their molecular weights measured with GPC were M_n = 71,000 and M_n = 120,700, respectively.

The compatibilizer, St-*g*-PLLA, was synthesized and characterized as described in our previous article[31]: the starch surfaces were first modified by reacting the hydroxyl groups on the starch with L-lactic acid, and then the St-*g*-PLLA was synthe-

TABLE I
Starch/PCL Blends and Their Thermal Analysis Data

Sample entry	St-*g*-PLLA$_{64}$ Content (wt %)	T_m (°C)	ΔH_m (J/g)	X_c (%) of PCL
1	2	59.1	65.1	47.9
2	5	59.3	65.9	48.5
3	10	60.2	67.4	49.6
4	20	58.7	63.0	46.3
Starch/PCL	0	57.6	56.7	41.7
PCL	0	61.5	69.2	50.9

The weight ratio of starch and PCL is 50 : 50 for all blend samples. St-*g*-PLLA$_{64}$ was used as compatibilizer. Its content is with respect to the total weight of PLLA and starch.

sized *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. After the polymerization reaction, the unreacted LLA monomers and PLLA homopolymer were washed off with ethanol and toluene, respectively. In the previous article,[33] it was concluded that with increase of the PLLA chain grafting rate, the interfacial tension between starch and PLLA also increased. So in this study, a St-*g*-PLLA with PLLA grafting rate of 64% (St-*g*-PLLA$_{64}$) was selected as the compatibilizer.

PCL/starch blend preparation

The PCL/starch blends with various St-*g*-PLLA$_{64}$ contents shown in Table I were prepared by mixing the three components in an internal mixer (Haake) at 140°C for 15 min. And then, the cooled mixture was molded into 1–2 mm thick sheets by hot-pressing at 120°C. PCL/starch blends without compatibilizer were made undert the same processing conditions for comparison.

Thermal analysis of the composites

The thermal characteristics and crystallinity of PCL component in the blend were evaluated by differential scanning calorimetry (DSC) and wide angle X-Ray diffraction (WAXD). The DSC analysis was performed at a heating rate of 10°C/min under N$_2$ atmosphere on a Perkin Elmer Pyris 1 instrument. Crystallinity of the PCL in the composites was calculated from the following formula[34]:

$$\text{Crystallity (\%)} = \Delta H_M / 136 \times 100\%$$

where ΔH_M is the melting enthalpy (in J/g) calculated from the fusion peak of DSC (the second heating run). And the value 136(J/g) is the theoretical enthalpy of completely crystalline PCL.

The WAXD analysis was conducted with a Philips apparatus using a Cu Kα(λ = 0.154 nm) source. Measurements of the diffracted intensities were made in the angular range of 5°–50° (2θ) at room temperature and at a scan rate of 1°/min.

Phase separation test

To isolate a mixed starch/PCL phase, the selective extraction of the components has been carried out on the starch/PCL/10% St-g-PLLA$_{64}$ and on the starch/PCL as reference.[35] Samples have been suspended in chloroform to form emulsions. Then, the emulsion was put in a cylindrical separator funnel and left at room temperature for 24 h to let the phase segregate according to a procedure known as "Molau test."

Tensile strength

Tensile strength and elongation at break were determined at room temperature on an Instron 1121 tester at a constant deformation rate of 5 mm/min. A minimum of three specimens were tested, and the results were averaged. The dumbbell-shaped specimens for tensile measurements were cut from the sheets in accordance to ASTM Standard D638 V.

Thermo-mechanical analysis

Thermo-mechanical properties of the different blends were measured by a dynamic thermo-mechanical analyzer (Metravib Mak-04 Viscoanalyser). Specimens with dimensions of 20 mm × 4 mm × 2 mm were cut from the central part of the sheets. They were tested by applying a bending constraint using the dual cantilever geometry. The displacement amplitude was set to 3 μm. The measurements were performed at a frequency of 11 Hz. The temperature range was from −80 to 60°C at the scanning rate of 3°C/min.

SEM observation

The starch/PCL blend morphology was investigated by a Model XL 30 ESEM FEG from Micro FEI Philips after sputter-coating of gold on the fractured surface of the dumbbell specimens.

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.

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 corresponding aqueous solutions at room temperature for 24 h and measuring the weight loss of the films.

RESULTS AND DISCUSSION

The main limitation of the starch/PCL blends is lack of adhesion between the polysaccharide and the synthetic polymer matrices owing to their different polarity. In fact, starch and most of the hydrophobic polymers are immiscible. The simple blending usually produces a mixture with two separate phases. So, preparing a blend with excellent physico-mechanical property depends on a proper interfacial tension that generates a small phase size and strong interfacial adhesion to transmit an applied force effectively between the component phases. Compatibilization is the effective method to improve phase adhesion and to reduce interfacial energy between two immiscible phases. The compatibilization strategy is introduced by the addition of a premade block/graft copolymer composed of blocks that are each miscible with one of the homopolymers. These compatibilizers have turned several incompatible blends into compatible ones to improve their physical properties. The amphiphilic starch-g-poly(L-lacide) with a core-shell structure, with a core of hydrophilic starch and a shell of hydrophobic PLLA grafted, is expected to be a proper compatibilizer in starch/polyester blend.

Thermal analysis of the composites

The thermal properties of St/PCL blends with or without compatibilizer were summarized in Table I. The melting temperature (T_m), the fusion enthalpy (ΔH_m) and the crystallinity (X_c) of PCL in the blends was determined by DSC. Figure 1 showed the typical DSC curves of St/PCL blends. The pure PCL showed a T_m at 61.5°C and an X_c of 50.9% , and the St/PCL (50/50) blend showed a T_m at 57.6°C and an X_c of 41.7%. The addition of the starch decreased the T_m and X_c of PCL in the blend because the starch as filler in the continuous PCL phase restricted PCL crystallization. However, as the compatibilizer St-g-PLLA$_{64}$ was added into the blends, the values of T_m and X_c were all higher than that of the virgin St/PCL blends. This difference may be ascribed to the contribution of the St-g-PLLA filler. It was well
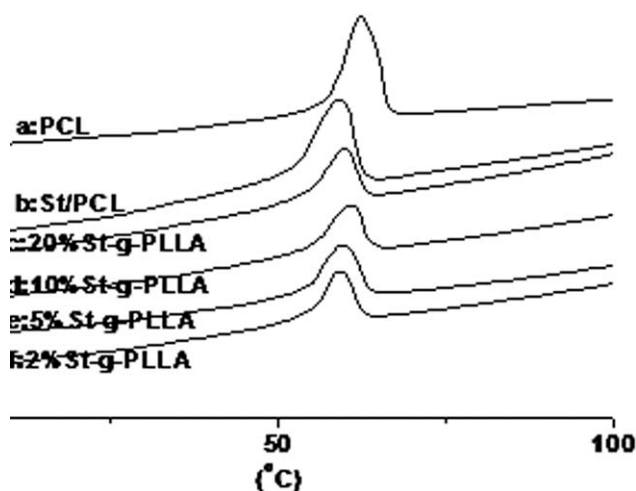
Figure 1 DSC curves (second heating run) of pure PCL (a), simple St/PCL blend (b), St/PCL with 20% St-g-PLLA (c), with 10% St-g-PLLA (d), with 5% St-g-PLLA (e), with 2% St-g-PLLA (f).

Figure 2 X-Ray curves of pure PCL (a), St/PCL/2%St-g-PLLA (b), and simple St/PCL blend (c).

known that the simple St/PCL blends usually showed depressed thermal properties because of the obvious phase separation and the weak interactions between the two phases. To enhance the interphase interactions, PLLA *grafted* starch is used as a compatibilizer in the starch/polyester blends. As shown in Table I, when the content of the compatibilizer increased from 2 to 15%, T_m and X_c of PCL in the blends increased correspondingly. Sample 3 displayed the maximum T_m and X_c. When the filler content of St-g-PLLA$_{64}$ reached 20%, the values of T_m and X_s all decreased a lot indicating that further increase of the compatibilizer is not suitable to the physical properties of the blends.

The crystallizability of the pure PCL, St/PCL blends with or without St-g-PLLA$_{64}$ could also be confirmed by WAXD patterns shown in Figure 2. The pure PCL [in Fig. 2(a)] showed two main diffraction peaks at $2\theta = 21.4°$ and $23.8°$, respectively. In Figure 2(b,c), there appeared peaks at 15.2°, 17.1°, and 23.1° attributed to starch crystal in the blends, especially in the blends with St-g-PLLA$_{64}$ as compatibilizer, which enhanced the interphase interactions between PCL and starch. There were no peaks attributed to PLLA, because in the blends the content of PLLA was too low. This result was accordant with that from DSC.

Phase separation test

By the "Molau test," it could observed that when virgin St/PCL blend was left at room temperature for a few minute, a complete phase separation with a supernatant starch phase and a clear CHCl$_3$ solution was reached, whereas in the case of St/PCL/10% St-g-PLLA$_{64}$ blend the solution was opaque
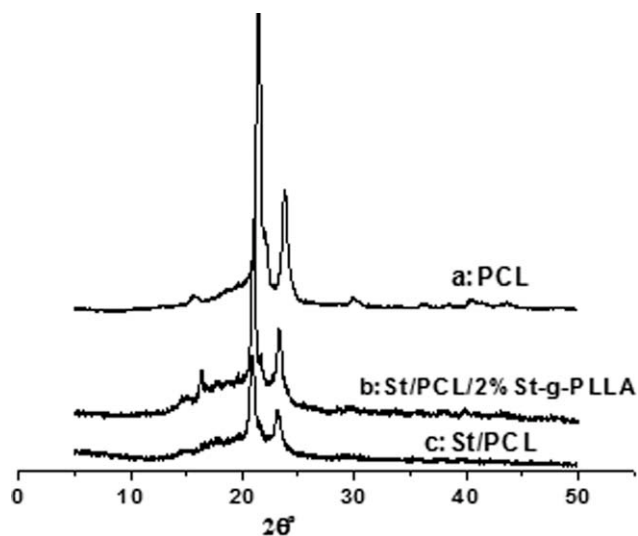
even after several weeks because of the suspension of St-g-PLLA$_{64}$. These phenomena clearly revealed the emulsifying effect of the St-g-PLLA$_{64}$. As matter of fact, the interfacial compatibility between starch and PCL was improved by St-g-PLLA$_{64}$.

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 (Fig. 3) and the related data are summarized in Table II. It was well known that the PCL was a ductile polymer with large deformations, but it had a relatively low modulus rendering it unable to be used for a high rigidity required applications. As expected, addition of starch fillers into PCL
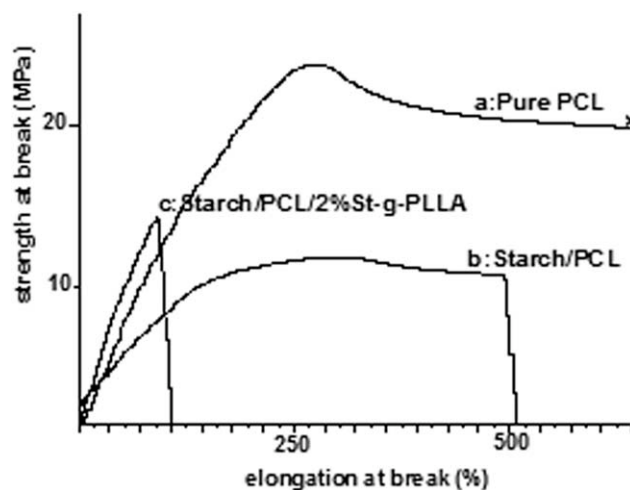

Figure 3 Typical stress-strain curves of PCL (a), simple starch/PCL blend (b), and starch/PCL with St-g-PLLA compatibilizer (c).

TABLE II
Tensile Properties of Starch/PCL Blend Compositions

Sample entry[a]	σ_b (MPa)	ε_b (%)	E (MPa)	σ_y (MPa)
1	13.7	125	798	7.6
2	15.2	131	813	8.8
3	16.6	139	996	9.2
4	15.1	127	862	8.4
Starch/PCL	8.0	516	597	3.9
PCL	31.8	1109	267	12.9

[a] The same samples as in Table I.
σ_b, strength at break; ε_b, elongation at break; E, tensile modulus; σ_y, strength at yielding.

matrix led to significant reduction of the σ_y, σ_b and ε_b because of the poor filler/matrix interfacial adhesion, but improved the blend modulus. The Young's modulus E of pure PCL was 267 MPa, whereas that of simple St/PCL was 597 MPa as twice as that of PCL. After addition of St-g-PLLA compatibilizer into the blends, the Young's modulus could reach to 996 MPa. The starch phases in the blends with or without compatibilizer acted as rigid filler not capable of being deformed in the blends. When the compatibilizer was incorporated into the blends, the mechanical properties were substantially improved. Concerning the mechanical behavior of St/PCL blends with the compatibilizer, the sample 3 containing 10% comaptibilizer presented a larger increase of elastic modulus accompanied by higher strength at yielding. On the contrary, the elongation at break decreased. These results were owing to the better interfacial adhesion between the starch and PCL. In the region of linear elasticity of the PCL matrix, the PCL chains could not move freely and then resuled in higher rigidity. That is to say, the PLLA *grafted* starch really played a role of compatibilizer because it was incorporated into both the PCL polyester phase and the starch phase. It did not only promote a better dispersion of the starch granules in the PCL matrix but also reinforced the adhesion between the fillers and the matrix hindered the moving of PCL macromolecules.

Generally, the properties of the blends depended on their morphology (phase structure) and the interfacial adhesion between starch and synthetic polymers. The scanning electron micrographs of uncompatibilized simple St/PCL blend [Fig. 4(a,c)] and
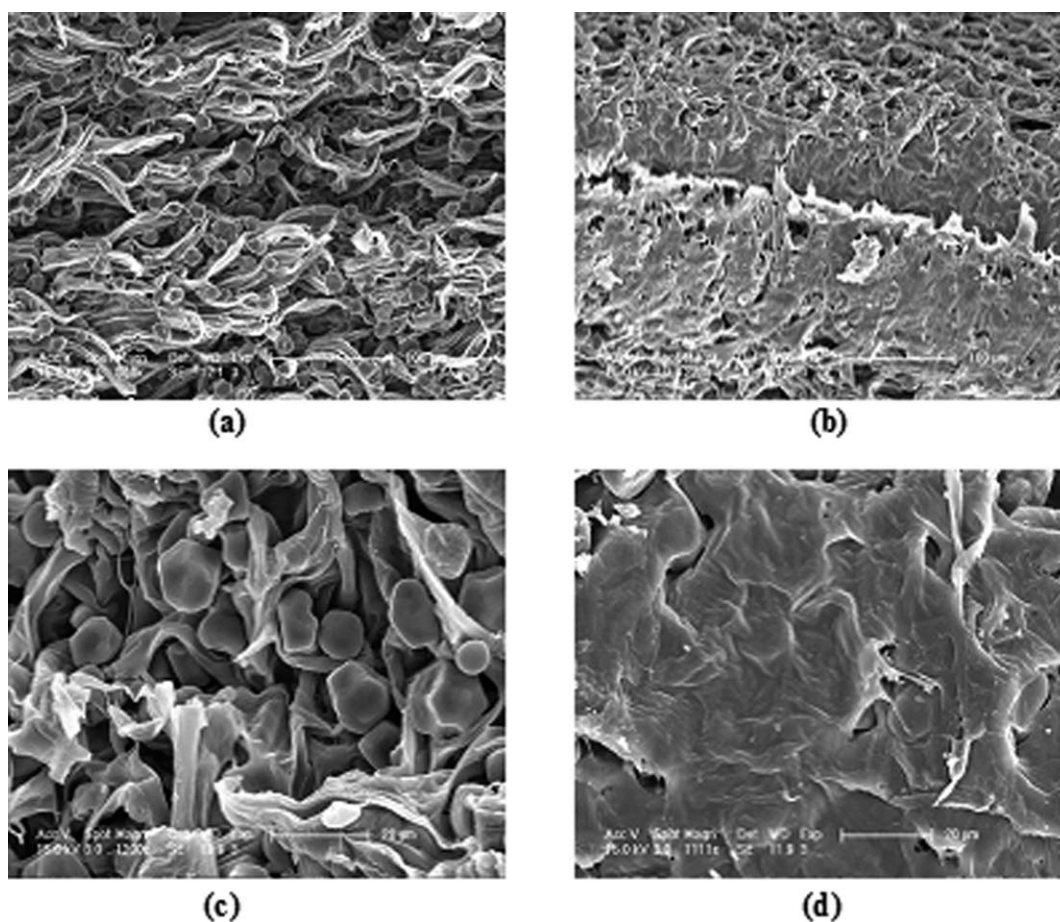

Figure 4   SEM micrographs of the fracture surfaces of the simple St/PCL blend (a), St/PCL/5%St-g-PLLA$_{64}$ (b), the magnified image of simple St/PCL blend (c), and the magnified image of St/PCL/5%St-g-PLLA$_{64}$ (d).

compatibilized St-*g*-PLLA/starch/PCL blend [Fig. 4(b,d)] performed on the fractured surfaces of the samples after the tensile test. It can be seen that the starch granules in the uncompatibilized blend were not homogeneously dispersed in the polymer matrix showing typical characteristics of an immiscible composite with poor interfacial adhesion [Fig. 4(a,c)]. A clear edge and aperture between the starch granules and PCL matrix were observed. However, in the blend containing 5 wt % compatibilizer [Fig. 4(b,d)], the starch granules were well dispersed within the polymer matrix and covered by PCL material, confirming a good interconnection between the starch granules and PCL matrix. The edge and the inter-phase between the two phases become blurry. Also, these blends showed an improved tensile strength, which indicates that the compatibilizer reduced the interfacial energy and thereby produced a finer and more uniform morphology.

Thermo-mechanical analysis

Figure 5 showed the storage modulus (E'), loss modulus (E''), and tan δ curves provided by dynamic thermo-mechanical analysis (DMTA) of pure PCL, uncompatibilized and compatibilized starch/PCL blends. In dynamic mechanical studies, changes occurred close to the T_g of the polymer, with the storage modulus decreasing rapidly with the increase of temperature from −80 to 0°C, and the loss modulus and tan δ showing maximal values at −60°C. In the transition region, these obvious changes were called as the primary dispersion (the α-peak). The magnitude of the α-peak in the amorphous polymer was much higher than in the semicrystalline polymer, primarily because of the chain segments of the amorphous polymer in the glass transition region. For pure PCL, there was a rapid decrease of the storage modulus with the increase of temperature at −60°C associated with a loss modulus peak and a tan δ peak which were consistent with a glass transition. A second transition is observed at higher temperatures (maximum of tan δ at 60°C), which could be associated with melting of the polymer.

For St/PCL blend and St/PCL/St-*g*-PLLA blend, the storage modulus at −80°C increased from 1900 MPa of pure PCL to 2370 MPa and 2940 MPa, respectively. The addition of 50 wt % starch to PCL particularly increased the storage modulus by enhancing the secondary forces of the St/PCL blends and made the blends more rigid than pure PCL by decreasing the polymer chain mobility. For all DMTA curves of the St/PCL blends with or without St-*g*-PLLA, a tan δ peak located at low temperature about −55°C to −57°C was observed. This peak corresponded to an overlapping of two signals: one
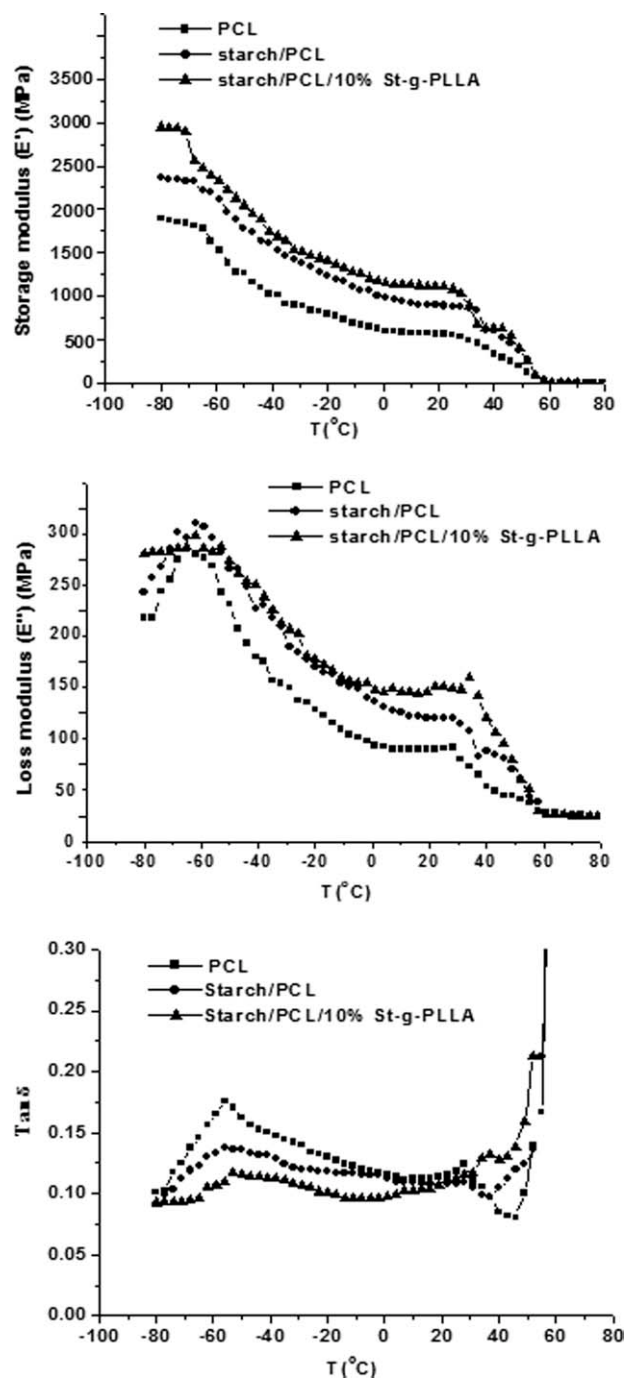

Figure 5 DMTA curves of PCL and starch/PCL blends with or without compatibilizer.

attributed to the glass transition of PCL and one arising from secondary relaxation of starch. The tan δ value at the α-peak was greater than at the dissipation peaks for lower temperatures and was accompanied by the greatest decrease in storage modulus with increasing temperature. The damping curve for the dynamic properties of heterogeneous copolymers reflected the border of the transition region between immiscible substances, and this transition was generally broad for such copolymers. As shown in Figure

5, the intensity of the tan δ peak decreased with the incorporation of starch, and the broad transition region observed indicated that PCL and starch were insoluble in each other. The lower intensity of tan δ seen in the blends indicated less movement of the molecular chains in the blends compared with pure PCL. It could include that the addition of starch increased the storage modulus of starch/PCL blends and decreased the glass transition temperature of PCL and the melt temperature of polymer blends. At the same time, the compatibilizer St-g-PLLA reduced the interfacial energy resulted in the increasing of storage modulus of the blends compared with simple St/PCL blend.

Contact angle measurements

The contact angle formed between a water droplet and a substrate surface, and the kinetics of spreading were related to the hydrophilic character of the material. The blends material's contact angle behaviors were quantitatively illustrated by the initial contact angle just after deposition of a droplet and by the evolution rate of the contact angle with time. The results were presented in Table III. For the pure PCL, the contact angle was 93° because of its hydrophobic nature. With the addition of the hydrophilic starch, the contact angle of the starch/PCL blends decreased to 51°. When St-g-PLLA compatibilizer was added to the blend, the value of the contact angle increased and this increase was dependent on the content of St-g-PLLA. For the simple St/PCL blend without the St-g-PLLA compatibilizer, the evolution rate of the water contact angle was more rapid than that with PLLA-g-St, because of the hydrophilic nature of the starch. When the St-g-PLLA was incorporated into the blends, the evolution slope of contact angle at the origin point became slower with time. In all cases, the introduction of St-g-PLLA leaded to a significant improvement of the material hydrophobicity. These behaviors provided further evidence for the improved compatibility or the reinforced adhesion between the starch

TABLE III
Contact Angle Measurements of St/PCL Blends

Sample entry[a]	Initial value (°)[b]	Slope at the origin (°/s)
1	68	−0.25
2	71	−0.2
3	72	−0.1
4	69	−0.1
Starch/PCL	51	−1.5
PCL	93	−0.05

[a] Sample entries 1–4 are referred as Table I.
[b] The data were collected by mean of five independent experiments.

TABLE IV
Medium-Resistance of the St/PCL Blends

	Weight change (wt %)		
Sample entry	In 0.5 mol/L HCl	In 0.5 mol/L NaOH	In H$_2$O
1	+5.2	−16.7	+5.9
2	+4.3	−16.1	+4.1
3	+3.6	−15.4	+3.4
4	+3.8	−15.8	+3.8
Starch/PCL	+18.3	−44.3	+19.5

The experiments of medium-resistance were carried out at room temperature.

granules and the PCL matrix in the St-g-PLLA compatibilized system. Because of the presence of the St-g-PLLA compatibilizer, the hydrophilic starch granules appeared to be hidden in the hydrophobic PCL matrix.

Medium-resistance

Water resistance was a very important factor for practical applications of starch-based materials, because starch was usually poor in storage stability for its sensitivity to moisture. The medium-resistances of the starch/PCL blends with or without St-g-PLLA to 0.5 mol/L acid solution, 0.5 mol/L alkaline solution and pure water were measured at room temperature (about 25°C) for 24 h, respectively. Dispersed in water or an acid solution, the films always gained a certain weights, whereas in an alkaline solution they lose weights at the beginning stage. The weight increase was because of the water adsorption by the starch in the blend and the weight-loss is because of the degradation of the starch catalyzed by the alkali. As shown in Table IV, the stabilities in all three media of the compatibilized blends were improved compared with the simple starch/PCL blend. Among them the blend with 10% of St-g-PLLA was the best.

CONCLUSION

The thermal, thermo-mechanical, and mechanical properties of starch/PCL blends with or without St-g-PLLA as campatibilizer have been investigated. The use of St-g-PLLA as a compatibilizer in starch/PCL blends can improve the performances without changing their whole biodegradability. St-g-PLLA is a good compatibilizer for the blend of hydrophobic PCL and hydrophilic granular corn starch. With the addition of St-g-PLLA, the tensile modulus of the blends increases because the starch acted as rigid filler, and St-g-PLLA improves interfacial adhesion and mechanical properties of the composites compared with the simple starch/PCL blend. At the

same time, the storage modulus of the starch/PCL blends also increase. These environmental compatible materials are characterized by less cost than the neat PCL and display all required qualities of a disposable plastic. Changing the amount of St-*g*-PLLA compatibilizer can tailor the properties of the composites for specific applications. Compared with the simple blend, the St-*g*-PLLA compatibilized starch/PCL blends show stronger water- and medium-resistance. Therefore, this kind of blend is an interesting approach to low cost biodegradable material in order, for instance, to increase the use of environmentally friendly materials in packaging industry or in fertilizer control release to be used as fertilizer carriers.

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