

Preparation and properties of compatible starch-polycaprolactone composites: Effects of molecular weight of soft segments in polyurethane compatilizer

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ABSTRACT: In this study, polycaprolactone (PCL)-diol samples of soft segment with different molecular weights were utilized to synthesize polyurethane prepolymer (PCLPUP) and was charged in an intensive mixer to prepare starch-PCLPU-PCL composites. The impact of the polyurethane soft segments with different molecular weights on the starch-PCLPU-PCL composite systems regarding their structure and properties, were thoroughly analyzed. Results showed that the PCLPU successfully increased the interaction between the starch and PCL in the composites, and can thus be used as an effective compatilizer to improve the compatibility between starch and PCL in the resultant composites. With decreasing molecular weight of PCLPU soft segments, the isocyanate group (NCO) content in the PCLPU increased, generating more urethane covalent bonds between PCLPU and starch, thereby enhancing the interaction between starch and PCLPU interface. Again, with decreasing molecular weight of PCLPU soft segments, the physical cross-linking between the PCLPU and PCL was increased, thereby enhancing the compatibility between PCL matrix and PCLPU interface. Owing to the improvement of compatibility between the starch filler and PCL matrix, the elongation and strength at break for the composite material likewise improved after the addition of PCLPU soft segments with low molecular weight. To this effect, a PCLPU soft segment with low molecular weight was added to the starch-PCL composites system to boost the overall performance of these starch-PCL composites. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 42381.

KEYWORDS: blends; composites; polyurethanes

Received 23 February 2015; accepted 19 April 2015

DOI: 10.1002/app.42381

INTRODUCTION

Under pressure from the worldwide, with increased environmental awareness during the past few years, many industries have endeavored to reduce their dependence of fossil fuels in enterprise products.¹ Environmentally friendly, renewable materials that replace existing oil-derived products have become a crucial consideration, and a common research goal.² Low-cost biodegradable material is a particularly hot topic in this area of study. Because starch is readily biodegradable and inexpensive, it is a highly favorable natural polymeric material.³ According to previous researchers, starch is one of the most promising environmentally friendly, renewable candidate materials for a variety of applications.⁴ However, the hydrophilic nature and brittleness of starch limit its potential utilization.⁵ These disadvantages can usually be resolved by blending the material with other polymers.

Previous studies have blended starch in conjunction with various biodegradable polymers to improve its performance.^{6–13} For

example, polycaprolactone (PCL) has been extensively studied due to its high toughness, hydrophobicity, and biodegradability. Moreover, it is known that the blended product of starch and PCL is completely biodegradable.¹⁴ However, poor compatibility between hydrophilic starch and hydrophobic PCL results in poor overall performance of starch-PCL composites.¹⁵ Increasing the materials' compatibility is thus the primary goal of researching starch-PCL composites.¹⁶ The use of a compatibilizing agent is considered an effective way to improve the compatibility between a variety of mixed materials, which improves the properties of the product by improving on the blending mechanisms. Thus, various compatibilizers have been used to improve the compatibility between starch and PCL, with mixed results.

Najemi *et al.* investigated the synthesis of biodegradable starch-graft-poly ϵ -caprolactone (starch-g-PCL).¹⁷ They used carbodiimidazole (CDI) as coupling agent to modify the PCL terminal groups, and then prepared starch-graft-poly ϵ -caprolactone

(starch-*g*-PCL) through a carbonate bond using carboimidazole function. The interfacial adhesion between the PCL matrix and starch dispersion phases dominated by the compatibilizing effects of the CDI was significantly improved. Duquesne *et al.* used a combination of *n*-butyl isocyanate, PCL-*g*-dextran (PGD), and PCL-*g*-granular starch (PGS) as an amphiphilic compatibilizer for starch-PCL blends.¹⁸ The compatibilized blends showed higher tensile strength and elongation at break compared with starch-PCL blends; however, most of the compatibilizers such as CDI do not efficiently react with PCL, and the graft efficiency of the modifiers will affect the compatibility between PCL and starch. Organic solvents such as dimethylsulfoxide (DMSO), toluene and tetrahydrofuran (THF) must have been used during modification, which inevitably results in rather serious environmental pollution. It however, remains highly necessary to find compatibilizers that are both effective and environmentally friendly to successfully improve the miscibility of starch-PCL blends.

Our research team, in a previous study,¹⁹ prepared polycaprolactone-based polyurethane prepolymer as a novel compatibilizer material to improve the compatibility between starch and PCL. The 70% quantity content of starch as the dispersed phase, dispersed in the 20% polycaprolactone continuous phase, as a result, the polycaprolactone was called the matrix. Multifunctional polyurethane was formed using the prior polycaprolactone matrix plus starch granules. The polyurethane prepolymer and starch were covalently cross-linked through urethane bonds, and the soft segment of the polyurethane and polycaprolactone in the PCL matrix were physically cross-linked. Thus, the starch-PCLPU-PCL composites prepared by adding polycaprolactone polyurethane prepolymer to starch compared with starch-PCL composites, showed significant improvement in mechanical properties and thermal stability. The method used is also a simple, efficient and environmentally friendly way of improving the compatibility between hydrophilic starch and hydrophobic PCL.

It is evident that polyurethane prepolymer is a major factor affecting the properties of starch-PCL composites. The molecular weight (M_w) of the soft segment in the preparation of polyurethane prepolymer is likewise an important factor of the material's performance. The reaction activity of polyurethane prepolymer and the mechanical properties of polyurethane are deeply associated with the soft segments of polyurethane prepolymer. Jimenez *et al.* found that with increasing molecular weight of the soft segment, changes in phase separation become apparent.²⁰ Previously, we used polyurethane prepolymer with soft segments of varying molecular weight to prepare modified starches, the structure and properties were directly affected by the polyurethane prepolymers.²¹ However, this effect of the interaction between the PCL matrix and PCLPU on the structure and physical properties of starch-PCL composites have not yet been explored.

In this study, various polyurethane prepolymers were synthesized using different molecular weights (M_w) of PCL diol. The polyurethane prepolymers were then mixed with starch and PCL mixture to prepare starch-PCL composites. The effects of the M_w of the soft segments of PUs on the structure and

properties of the resultant composites were investigated at length. The primary goal of this article is to further establish a series of new structure of compatibilizer and provide a clearer understanding of the impact of molecular weight of polyurethane soft segments on interface structure and properties of starch-PCL composites, in order to build a theoretical basis for the preparation of starch-PCL composites that exhibit exceptionally favorable performance.

EXPERIMENTAL

Materials

Polycaprolactone (CAPA[®] 6500, $M_w = 50,000 \text{ g mol}^{-1}$) and polycaprolactone diol (CAPA[®] 2077A, $M_w = 750 \text{ g mol}^{-1}$, hydroxyl value = $152.90 \text{ mg KOH g}^{-1}$; CAPA[®] 2100A, $M_w = 1000 \text{ g mol}^{-1}$, hydroxyl value = $113.36 \text{ mg OH g}^{-1}$; CAPA[®] 2200A, $M_w = 2000 \text{ g mol}^{-1}$, hydroxyl value = $57.52 \text{ mg KOH g}^{-1}$; CAPA[®] 2302A, $M_w = 3000 \text{ g mol}^{-1}$, hydroxyl value = $38.56 \text{ mg KOH g}^{-1}$) were purchased from Perstorp UK Ltd (Cheshire, UK). 4,4'-Methylenedi-*p*-phenyl diisocyanate (MDI, 98%) was purchased from Sigma-Aldrich Fine Chemicals (St. Louis, MO). Corn starch (CS, amylose: 23–26 wt %; moisture: 12 wt %) was obtained from Wuhan Corn Starch Co. Ltd (Wuhan, China) and used without alteration. Acetone (analytical grade) was purchased from the China National Pharmaceutical Group Corporation (Shanghai, China). Butyl acetate (analytical grade) was purchased from China National Pharmaceutical Group Corporation (Shanghai, China). Tetrahydrofuran (THF, 99%) was purchased from Shanghai Zhenxing No.1 Chemical Plant (Shanghai, China).

Synthesis of Polyurethane Prepolymer

The molar number ratio of isocyanate to hydroxyl group (NCO/OH) was 2.0. Polycaprolactone diol was charged into a 250 mL three-necked flask fitted with a stirrer operating at a speed of 300 rpm, with an inlet and an outlet. The diol was dried in a vacuum at 100°C to remove any moisture. After 30 min, the temperature of the PCL diol in the flask was lowered to 70°C. MDI was then added to the flask under vacuum conditions. The translucent mixture in the flask quickly became transparent. Fifteen minutes after the addition of MDI, the mixture was stirred vigorously and reacted at 80° for 1 h. Finally, a white Polyurethane Prepolymer (PUP) was obtained. 750 M_w of PCL diol was designated as PU750. With the same nomenclature, the 1000, 2000, and 3000 M_w of PCL diol samples were designated as PU1000, PU2000, and PU3000, respectively. The M_w of PU750, PU1000, PU2000, and PU3000 obtained from the GPC analysis were 7048, 8343, 9901, 11597 g mol^{-1} , respectively.

Gel Permeation Chromatography

Molecular weight and molecular weight distributions were measured using Gel Permeation Chromatography (GPC) (Agilent 1100, USA). The mobile phase selected was THF at a rate of 1.0 mL min^{-1} and the column temperature was maintained at 35°C. 10 different polystyrene samples with molecular weights ranging from 2000 to 5000,000 g mol^{-1} were used as standards. All the PU samples with different M_w of soft segments were prepared in THF and were subsequently used for GPC analysis.

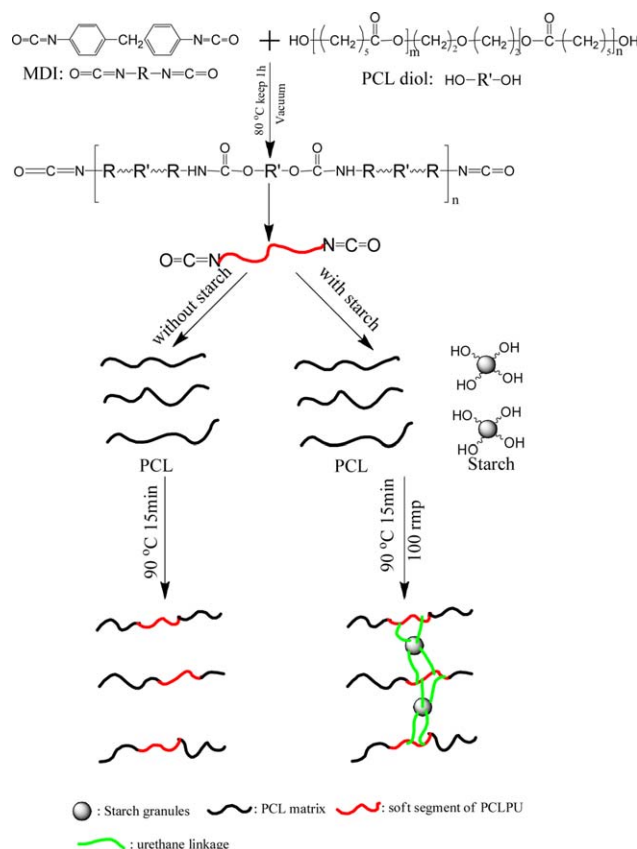


Figure 1. Reaction process of the composites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

NCO Content

NCO content was measured using the 2-dibutylamine method described in our previous study.²²

Preparation of PCL-PCLPU Blends

PCL (63 g) and PCLPU (7 g) were added to an intensive mixer (SU-70, Changzhou Suyan Science and Technology, Changzhou City, China) and mixed reactively at 90°C with a stirring speed of 100 rpm. After 15 min, a white PCL-PCLPU blend was obtained. The blends were equilibrated in a sealed plastic bag for 1 day before use. The blend consisting of PCL (90 wt %) and PU750 (10 wt %) was designated as PP750. With the same procedure, PU1000, PU2000, and PU3000 were used to prepare PP1000, PP2000, and PP3000 samples, respectively.

Preparation of Starch-PCL Composites

Corn starch (49 g), PCLPU (7 g) and PCL (14 g) were added to an intensive mixer (SU-70, Changzhou Suyan Science and

Technology, Changzhou City, China) and mixed reactively at 90° with a stirring speed of 100 rpm. After 15 min, a white starch-PCL composite was obtained. The composite was equilibrated in a sealed plastic bag for 1 day before use. The composite consisting of corn starch (70 wt %), PU750 (10 wt %) and PCL (20 wt %) was designated as CPP750. With the same procedure, PU1000, PU2000, and PU3000 were used to prepare CPP1000, CPP2000, and CPP3000 samples, respectively. The composite consisting of corn starch (70 wt %) and PCL (30 wt %) was designated as CP (A diagram of the synthesis procedure is shown in Figure 1 and a diagram of the flow chart is shown in Figure 2).

Fractionation of the Composites

Purification of Starch-PCL Composites. To analyze the structure of the components in starch-PCL composites, the PCL fraction was first extracted from the composites using acetone. CPP750 (10 g) and acetone (200 g) were added into a 500 mL three-necked flask fitted with a stirrer operating at a speed of 300 rpm. The composite was dispersed at 55°C for 1 h. After the dispersion, it was centrifuged at 8000 rpm in a centrifuge (Shanghai Anting Scientific Instrument Factory, Shanghai, China) for 10 min, the supernatant obtained was PCL-acetone solution. The acetone was then added into the precipitate to further extract the PCL component three times. After the PCL-acetone solution was concentrated, the concentrated PCL and the precipitate were vacuum dried at 40° for 12 h to obtain extracted modified starch (CPR750). We also adopted the same method to extract PCL from CP using acetone and obtained extracted starch (CPR). Further specifications of the sample abbreviations are shown in Table I.

Preparation of Sample Sheets by Compression-Molding

Starch-PCL composites were compression-molded using a hot press (R3202 model, Wuhan Qien Science and Technology, Wuhan, China) equipped with a water cooling system. The molding time, temperature and pressure were 5 min, 90°C, and 40 MPa, respectively. The sheets were cut into dumbbell-like shapes (5A type) according to GB/T1040-2006 standards. The length of each dumbbell-like specimen was 75 mm, and the widths of the narrow section were 4 mm. The sheets were equilibrated at 60% RH for at least 2 weeks before testing.

X-ray Diffraction

The composite sheets were measured using wide angle X-ray diffraction (WAXRD) (Y-2000 Dandong Radiative Instrument Group, China). For irradiation, the Cu K α line was applied (λ at 0.1542 nm, cathode at 30 kV and 20 mA) and scattering was recorded as 2θ in a range from 2 to 40°.

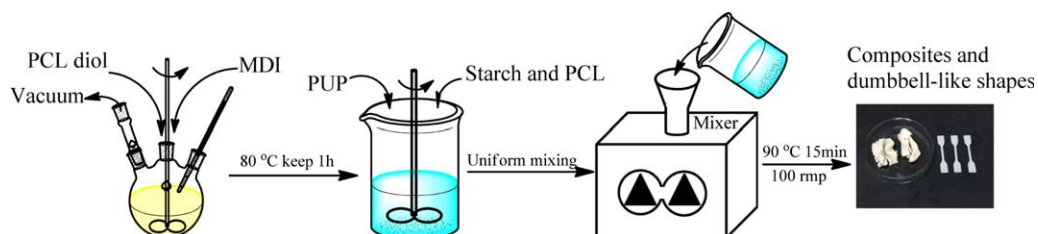


Figure 2. Flow chart of the composites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table I. Specifications of the Sample Abbreviations

Abbreviation	Specification	Abbreviation	Specification
PCL	Polycaprolactone	CS	Corn starch
PCLPU	PCL-based polyurethane prepolymer	CP	Starch-PCL composite (mass ratio of CS and PCL is 70 : 30)
PU750	PCL-based polyurethane prepolymer using 750 M_w of PCL diol	CPP750	Starch-PCL composite with PU750 compatibilizer (mass ratio of CS, PCL and PU750 is 70 : 20 : 10)
PU1000	PCL-based polyurethane prepolymer using 1000 M_w of PCL diol	CPP1000	Starch-PCL composite with PU1000 compatibilizer (mass ratio of CS, PCL and PU1000 is 70 : 20 : 10)
PU2000	PCL-based polyurethane prepolymer using 2000 M_w of PCL diol	CPP2000	Starch-PCL composite with PU2000 compatibilizer (mass ratio of CS, PCL and PU2000 is 70 : 20 : 10)
PU3000	PCL-based polyurethane prepolymer using 3000 M_w of PCL diol	CPP3000	Starch-PCL composite with PU3000 compatibilizer (mass ratio of CS, PCL and PU3000 is 70 : 20 : 10)
PP750	PCL-PCLPU blend using PU750 (mass ratio of PCL and PCLPU is 9 : 1)	PP1000	PCL-PCLPU blend using PU1000 (mass ratio of PCL and PCLPU is 9 : 1)
PP2000	PCL-PCLPU blend using PU2000 (mass ratio of PCL and PCLPU is 9 : 1)	PP3000	PCL-PCLPU using PU3000 (mass ratio of PCL and PCLPU is 9 : 1)
CPR	Residue of CP extracted with acetone	CPR750	CPP750 residue extracted with acetone

Emission Scanning Electron Microscopy

An Emission Scanning Electron Microscopy (ESEM) (FEI, Quanta 200 FEG, Netherlands) was used to observe the cross sections of the fractured samples. Each sample was frozen using liquid nitrogen and then fractured using tweezers to produce cross-sections. The cross-sections were coated with gold prior to ESEM observation.

Differential Scanning Calorimetry

The Differential Scanning Calorimetry (DSC) experiments (Diamond DSC, PerkinElmer Instruments, Waltham, MA) were conducted in a nitrogenous atmosphere. The system was calibrated with indium, and then about 10 mg of the sample was placed in an aluminum pan and sealed. The specimens were heated from 30 to 110°C at a rate of 10°C min⁻¹ (first heating scan), then equilibrated at 110°C for 2 min and cooled rapidly at 10°C min⁻¹ to -50°C, then equilibrated at -50°C for 2 min and finally heated again to 100°C at 10°C min⁻¹ (second heating scan). The melting point (T_m) was then determined on the second scan at the midpoint of the calorific capacity change on the thermogram. Enthalpy (ΔH_m) value was then utilized to calculate the degree of crystallinity by comparing ΔH_m with that of completely crystalline PCL according to the following equation.

$$\chi_c = \frac{\Delta H_m}{\Delta H_0} \times 100\%$$

where ΔH_0 is the melting enthalpy of completely crystalline PCL and is taken as 139.5 J g⁻¹.²³

Dynamic Mechanical Analysis

Dynamic Mechanical Analysis (DMA) was performed using a dynamic mechanical analyzer (DMA Q800, TA Instruments, New Castle, DE) in the single cantilever mode. The starch-PCL

composites samples were investigated from -110 to 40°C at a heating rate of 5°C min⁻¹ because the samples melted above 40°C. A variable-amplitude sinusoidal tensile stress with a frequency of 1 Hz was applied to the samples to produce a sinusoidal strain of 15 mm amplitude. The temperature at the peak of the $\tan \delta$ curve ($T_{\tan \delta}$) was considered the glass transition temperature (T_g) of each samples.

Mechanical Test

The mechanical properties of the composites were assessed by determining their tensile properties. Tensile properties were measured using a tensile tester (CMT6503, Shenzhen SANS Test Machine, Shenzhen, China). The samples cut from molded sheets were aged at 60% RH in room temperature for 2 weeks. Tensile properties were then measured using the tensile tester with a strain rate of 5 mm min⁻¹. The distance between the two clamps was 40 mm. Strength at break (σ_b , MPa) and elongation at break (ϵ_b , %) of the sheets were recorded. Measurements were gathered five different times for each sample.

Thermogravimetric Analysis

Testing was conducted using a thermogravimetric analyzer (STA 449 C, Netzsch Instruments Inc. Burlington, MA). Approximately 10 mg of sample cut from each sheets were equilibrated under ambient conditions and then subjected to heating from 30 to 600°C at a rate of 10°C min⁻¹ in a nitrogen atmosphere. Weight losses with respect to temperature were recorded.

RESULTS AND DISCUSSION

Structure

The NCO contents of PU750, PU1000, PU2000, and PU3000 obtained as 6.8% ± 0.1, 5.5% ± 0.1, 3.4% ± 0.2 and 2.4% ± 0.1,

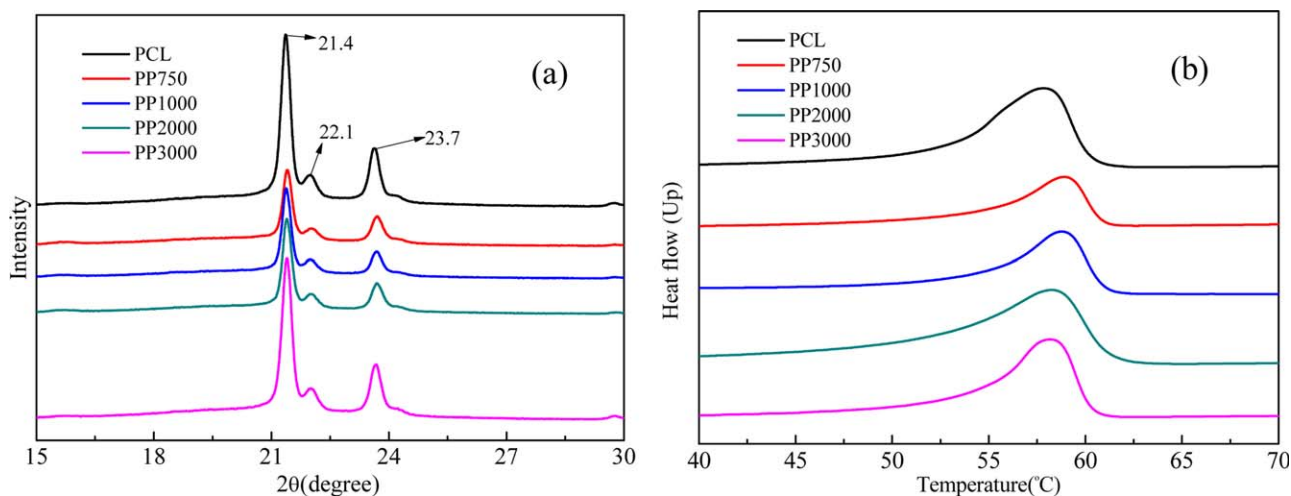


Figure 3. (a) WXR D pattern of PCL, PP750, PP1000, PP2000, and PP3000; (b) DSC thermogram for PCL, PP750, PP1000, PP2000, and PP3000. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

were closed to the theoretical value (6.7%, 5.6%, 3.4%, and 2.4%, respectively). These results indicated that the reaction for synthesizing PUP had reached its end point and that the NCO contents were increased with decreasing molecular weight of PCLPU soft segments.

WXR D spectra and typical DSC curves of the PCL-PCLPU blends are shown in Figure 3 and the T_m and χ_c of DSC are shown in Table II. Figure 3(a) shows the WXR D pattern of PCL and PCLPU blends with soft segments of different molecular weights. For pure PCL samples, there are three peaks at 21.4, 22.1, and 23.7°, each corresponding to the crystallization of PCL.²⁴ After adding PCLPU, the intensities of these peaks for PCL-PCLPU were significantly reduced, these were attributed to the soft segments of PCLPU interacting with the crystals of PCL through crystallization and producing physical cross-linking between the PCLPU and PCL matrix, which resulted in decreased activity of the molecular chains in the PCL matrix and reduction of crystalline properties. With increasing molecular weight of PCLPU soft segment, the intensity of the three crystallization peaks of the samples tended to increase, thereby illustrating that as the molecular weight of PCLPU soft segment increased, there were less physical cross-linking between the PCLPU and PCL matrix, and reduced interaction forces, resulting in a smaller impact on the crystallization behavior of PCL. When the molecular weight reached 3000, the interaction between PCL and PCLPU was very weak, namely PCLPU had little effect on the crystallinity of PCL, therefore the PP3000 showed similar peak intensities with that of PCL.

Figure 3(b) shows the DSC maps for PCL and PCLPU blends with soft segments of different molecular weights. For pure PCL samples, the T_m was 57.8°C.²⁵ After adding PCLPU, the T_m of PCL-PCLPU blends increased while the χ_c decreased, thereby illustrating that the addition of PCLPU increase the interaction between PCL chain and PCLPU chain, resulting in a shift of PCL T_m peak to a higher temperature. However, due to the existence of MDI hard domains, the PCL crystals were partially destroyed, resulting in a reduction in ΔH_m . As shown in

Table II, increasing molecular weight of the PCLPU soft segments caused increased χ_c value. This result is consistent with XRD observations. By combining the findings of Figure 3 and Table II, it becomes clear that the interaction between PCL and PCLPU weakens with increase in molecular weight of PCLPU soft segments.

SEM micrographs of the fractured surfaces of CP, CPP750, CPP1000, CPP2000, CPP3000, CPR, and CPR750 are shown in Figure 4(a–g). Figure 4(a), clearly shows that the starch granules had been pulled out from the PCL matrix during preparation by the process of brittle fracture, forming several cavities on the PCL matrix. In other words, there were weak interactions between the starch granules and the PCL matrix.²⁶ Upon addition of PCLPU to the starch-PCL composite system [Figure 4(b)], the starch granules wrapped in the inner layer and produced no obvious gaps or cavities between the starch and PCL. Thus, PCLPU is demonstrably effective for starch-PCL composite systems, as addition of PCLPU compatibilizer improved the compatibility between the starch granules and PCL matrix of the samples. Cavities began to appear in the surface of the PCL matrices when molecular weight of PCLPU increased. This shows that with the increase in molecular weight of PCLPU soft segment, PCLPU weakened the compatibility between starch and PCL, starch particles were drawn out of the PCL matrix surface, leaving cavities behind [Figure 4(c–e)]. With increased molecular weight of the PCLPU soft segments, the number of cavities also gradually increased, demonstrating that increased

Table II. ΔH_m , T_m , and χ_c for PCL, PP750, PP1000, PP2000, and PP3000

Sample	ΔH_m (J/g)	T_m (°C)	χ_c (%)
PCL	55.7	57.8	39.9
PP750	43.9	58.9	31.5
PP1000	44.5	58.7	31.9
PP2000	47.2	58.2	33.8
PP3000	51.8	58.1	37.1

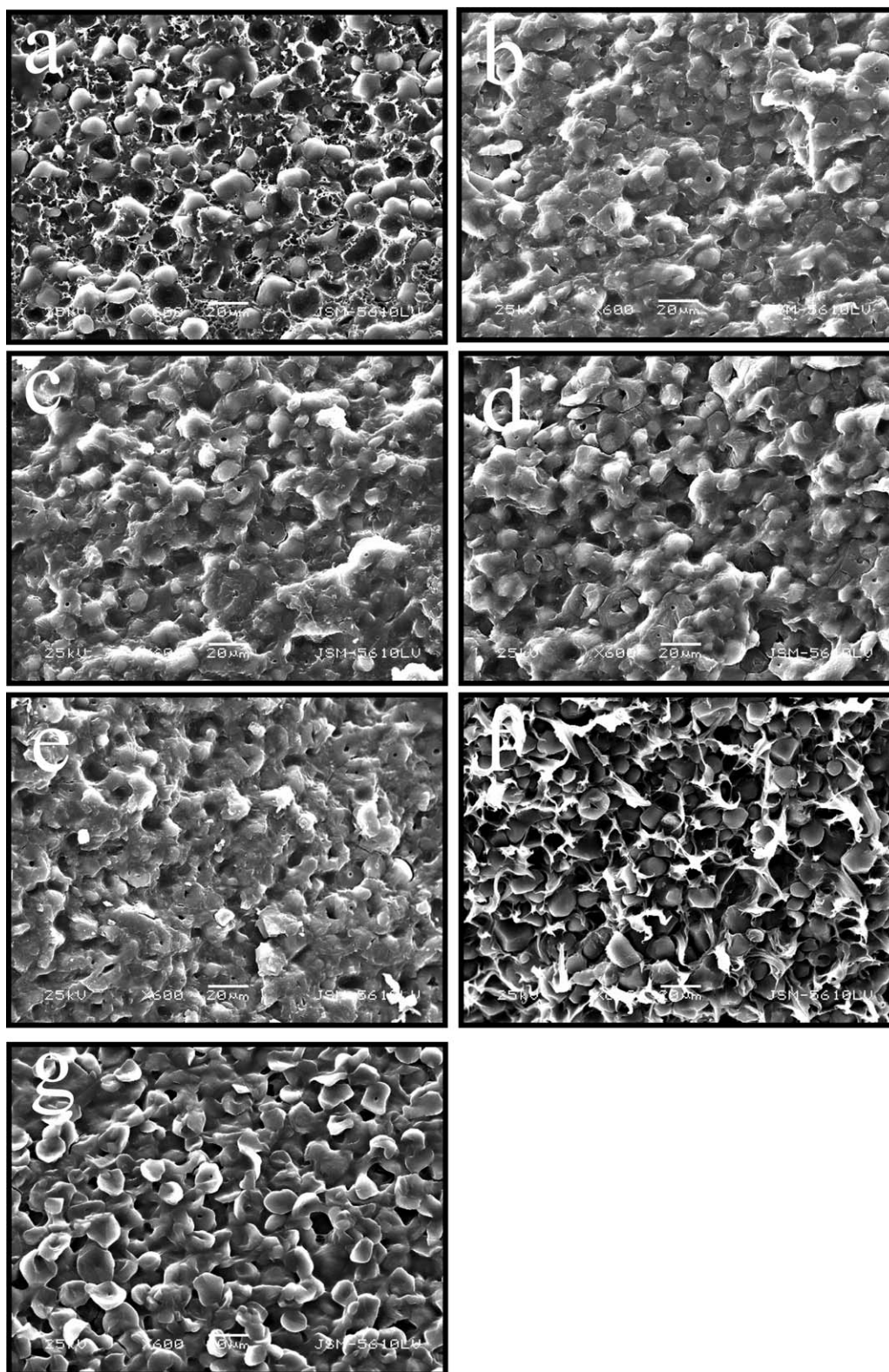


Figure 4. SEM micrographs of CP composite, CPP750 composite, CPP1000 composite, CPP2000 composite, CPP3000 composite, CPR residue, and CPR750 residue.

PCLPU segment molecular weight decrease the amount of interaction between starch particles and the PCL matrix. This occurs mainly due to the changes in the NCO content of the PCLPU.²⁷

With increased molecular weight of PCLPU soft segments, the NCO content decreases, resulting in few urethane bonds between the starch granules and the PCLPU, thereby, reducing

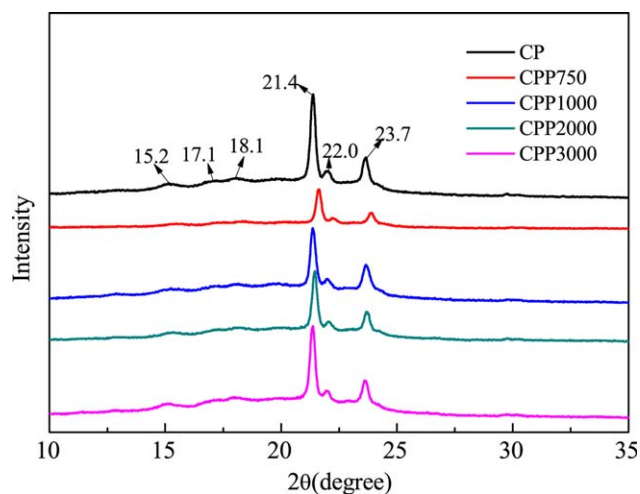


Figure 5. WXR D pattern of CP, CPP750, CPP1000, CPP2000, and CPP3000. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the total interaction between the starch particles and PCL matrix. As shown in Figure 4(f), small amount of residual PCL were present around the starch granules and the starch hydroxyl groups formed hydrogen bonds with the carbonyl groups in the PCL matrix.^{6,7,16} Basically, the PCL was not removed completely from the starch granules by acetone. From Figure 4(g), it clearly shows that the morphology of the starch particles changed, and that wide PCL matrix surface was wrapped with starch granules. The reaction between starch hydroxyl groups and PCLPU isocyanate groups formed urethane covalent bonds. At the same time, the strong interaction between PCLPU and PCL matrix made it difficult for the PCL to be removed completely from the surface of the starch granules using acetone; the addition of PCLPU did not only improve the interaction between starch and PCL, but also improved the compatibility between the starch particles and the PCL matrix. Moreover, with decreased

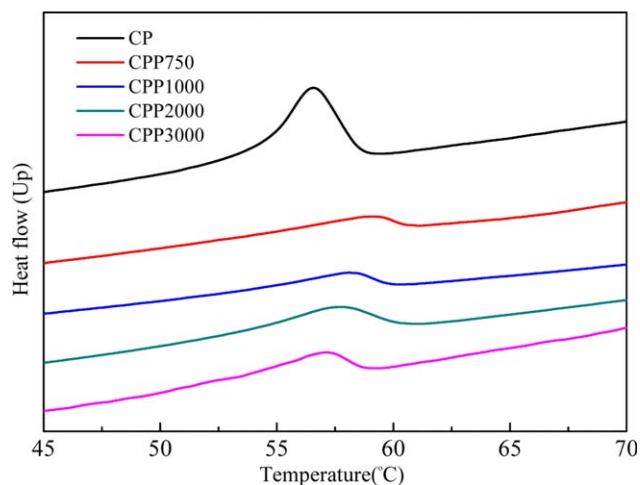


Figure 6. DSC thermogram for CP, CPP750, CPP1000, CPP2000, and CPP3000. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table III. ΔH_m , T_m , and χ_c for CP, CPP750, CPP1000, CPP2000, and CPP3000

Sample	ΔH_m (J/g)	T_m (°C)	χ_c (%)
CP	11.8	56.5	8.5
CPP750	4.8	59.3	3.4
CPP1000	5.2	58.4	3.7
CPP2000	6.7	57.8	4.8
CPP3000	7.1	57.1	5.1

molecular weight of PCLPU soft segments, the compatibility between the starch particles and the PCL matrix showed an increasing trend.

WXR D spectra for CP, CPP750, CPP1000, CPP2000, and CPP3000 samples are shown in Figure 5. The crystallization peaks of PCL for sample CP were 21.4, 22.0, and 23.7 and the crystallization peaks for typical A-type starch were 15.2, 17.1, and 18.1.^{28–30} Compared with CP, the intensity of crystallization peaks in all six samples decreased as PCLPU was added, due in part to the urethane covalent bonds between starch and PCLPU reducing the strength of the starch crystallization peaks, and partially because the interactions of the starch worsened the mobility of the PCL molecular chains, reducing the crystallinity of PCL and thus the intensity of the crystallization peaks decreased. The intensity of each crystallization peak for any of the samples increased alongside increasing molecular weight of PCLPU soft segments. It can thus be inferred that with increased PCLPU soft segment molecular weight, the interaction between starch and PCL in the composite worsened. This occurred for two primary reasons: first, as the molecular weight of PCLPU soft segments increased, the NCO group content is reduced, reducing the interaction between starch and PCLPU, and second, as shown in Figure 5, the interaction between PCL and PCLPU reduced under increasing molecular weight of the PCLPU soft segment.

Thermal Properties

The typical DSC curves for CP, CPP750, CPP1000, CPP2000, and CPP3000 samples are shown in Figure 6, the T_m and χ_c values obtained from DSC are shown in Table III. In the CP sample, the T_m peak of pure PCL was 56.5°C.³¹ After addition of PCLPU, the T_m of each starch-PCLPU-PCL composite was higher compared to the T_m of the starch-PCL composite without PCLPU, because the addition of PCLPU improved the interaction between starch and PCL, the mobility of PCL molecular chains was reduced, and thus, the melting peak of PCL in the composites was weakened and widened. Furthermore, after adding PCLPU soft segments of varying molecular weights, the T_m of the composites decreased and χ_c increased with increased molecular weight. To this effect, it is clear that as the molecular weight of PCLPU soft segment increased, the interaction between starch and PCL weakened, resulting in T_m and χ_c values similar to composites without any PCLPU added. All in all, adding PCLPU soft segments of low molecular weight to the composites resulted in a much stronger interaction between the starch and PCL.

Figure 7 shows the DMA curves of the CP, CPP750, CPP1000, CPP2000, and CPP3000 samples. In sample CP, the peaks at

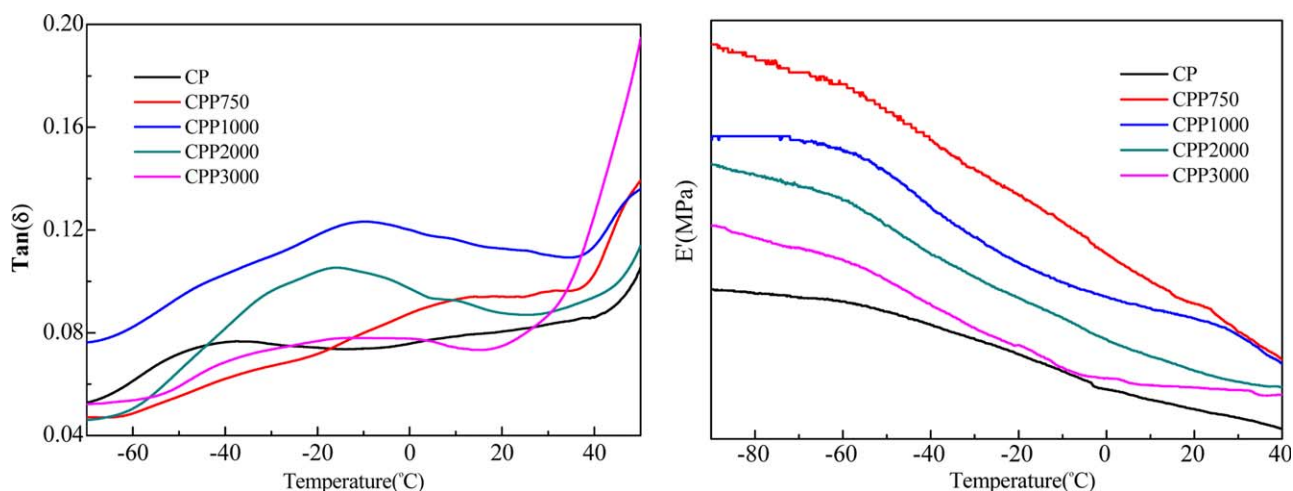


Figure 7. $\tan \delta$ and storage modulus (E) curves of CP, CPP750, CPP1000, CPP2000, and CPP3000. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

-45.7°C correspond to the glass transition temperature of the PCL matrix in the composite.³² After addition of PCLPU, the glass transition temperature of the samples increased because PCLPU enhanced the interaction between starch and PCL and inhibited the mobility of PCL molecular chains. After adding PCLPU soft segments with varying molecular weights, the T_g of the composites decreased as the soft segment molecular weight increased. The T_g of CPP750 and CPP3000 was 5 and -20°C , respectively, because, the hard segment content in PU3000 was less than that in PU750, there were less chemical bonds between starch and PU3000. In addition, the physical crosslinking between PU3000 and PCL was less than that of PU750 and PCL. As a result, the mobility of PCL molecular chains was increased and the T_g of PCL shifted to a lower temperature in CPP3000. Therefore, as the molecular weight of PCLPU soft segments increased, the interaction between polyurethane and PCL became weak, and the polyurethane chains became flexible, resulting in the lower T_g for higher molecular weight of soft segments.³³ Regarding the

storage modulus, after addition of PCLPU, the composite material grew stronger with decreasing soft segments molecular weight. Moreover, the storage modulus also shows that the addition of PCLPU soft segments with lower molecular weights resulted in a stronger interaction between starch and PCL.

Figure 8 shows the thermogravimetric analysis (TGA) curves of the CP, CPP750, CPP1000, CPP2000, and CPP3000 samples. The thermal degradation of the composite material is divided into four distinct phases. At the first stage, from room temperature to about 150°C , all the samples lost about 5% of their mass due to evaporation of their moisture content.³⁴ At the second stage, from 280 to 350°C , the curves for all composites exhibited the same trend due to the thermal decomposition of starch macromolecules.³⁵ At the third stage, from 350 to 390°C , the CP sample showed higher quality than sample CPP, owing to the thermal decomposition of MDI components in the hard segments of PCLPU in the composite.³⁶ With increasing molecular weight of PCLPU soft segment, CPP residual mass increased due to lower MDI content in the PCLPU hard segment, which contained soft segments of high molecular weight. The fourth stage, from 390 to 600°C corresponds to the thermal degradation of PCL and PCLPU soft segment.^{37–39} The quality of sample CPP was higher than the CP samples, demonstrating that the physical cross-linking between PCLPU and the PCL matrix improved the thermal stability of the complexes.

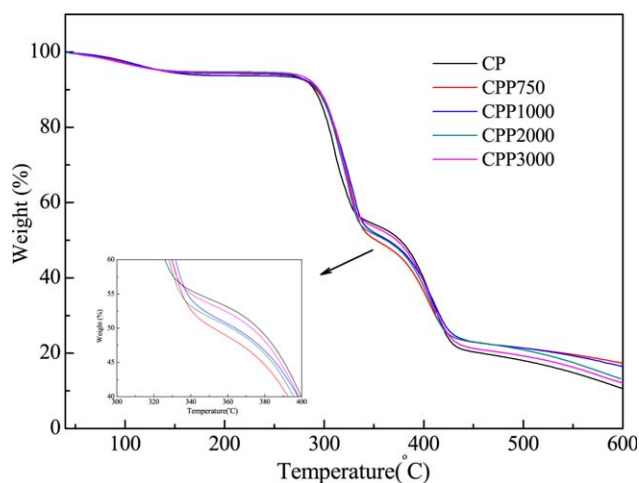
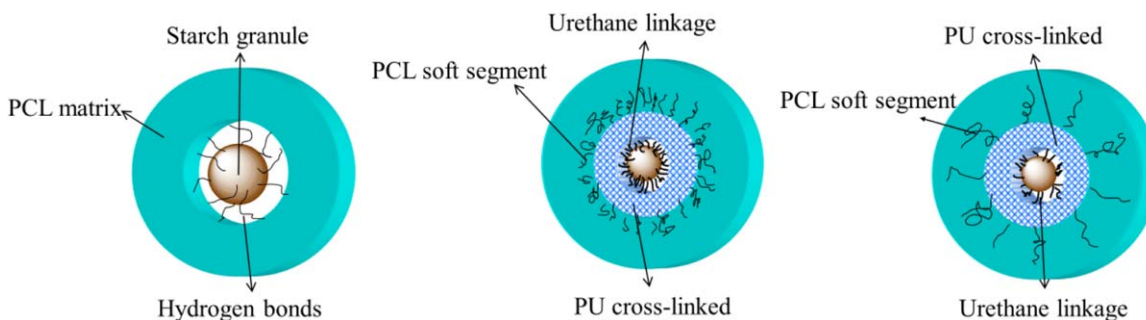


Figure 8. TGA thermograms of CP, CPP750, CPP1000, CPP2000, and CPP3000. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table IV. The Mechanical Properties of Molded Composites Sheets of CP, CPP750, CPP1000, CPP2000, and CPP3000

Sample	Tensile test		
	σ_b (MPa)	ϵ_b (%)	E (MPa)
CP	5.9 ± 0.1	0.8 ± 0.1	963.7 ± 67.9
CPP750	33.9 ± 1.5	17.7 ± 2.5	1056.8 ± 32.6
CPP1000	27.2 ± 0.7	10.9 ± 2.4	1065.8 ± 58.2
CPP2000	25.7 ± 1.3	5.9 ± 0.7	1314.3 ± 52.9
CPP3000	24.1 ± 0.4	4.3 ± 0.3	1615.3 ± 116.0



Scheme 1. Schematic diagram of different between CP, CPP750, and CPP3000. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Comparative analysis of the CPP samples showed that with increasing molecular weight of PCLPU soft segments, the quality of resultant samples decreased. For PCLPU soft segments of higher molecular weight, the soft segments also have a higher mass, thereby resulting in a greater mass that must undergo thermal degradation.

Mechanical Properties

The mechanical properties of the composites were determined through tensile measurements, results of which are listed in Table IV. The CP samples exhibited a significantly low elongation at break $0.8\% \pm 0.1$ and had very low strength at break $5.9 \text{ MPa} \pm 0.1$, due to the poor compatibility between starch and PCL resulting in weak interactions and weak mechanical strength. After the addition of PCLPU, the elongation at break of the composite material increased from 4.3 to 17.7%, and the strength at break increased from 24.1 to 33.9 MPa. These indicate that the addition of PCLPU effectively improves the compatibility between starch and PCL, thus increasing the mechanical strength of the resultant composite material. Along with decreasing molecular weight of PCLPU soft segments, the elongation rate increased from 4.3 to 17.7% and the strength at break increased from 24.1 to 39.9 MPa, further demonstrating that, the addition of PCLPU soft segments with lower molecular weight strengthened the interaction between starch and PCL. The CPP750 had a lower elastic modulus than CPP3000 but the storage modulus was different due to the higher elongation at break in CPP750 than that in CPP3000. The strength at break had no obvious changes which indicate that, CPP750 was flexible and soft while CPP3000 was crisp and rigid. As a result, CPP3000 showed a higher elastic modulus than CPP750. These results are consistent with the aforementioned XRD, SEM, DSC, and TGA analyses. In addition, the mechanical strength improved partly due to the chemical cross-linking via covalent bonds between starch and PCLPU, and also due to the physical cross-linking between PCLPU and coexisting PCL crystals. With increased PCLPU soft segment molecular weight, the chemical cross-linking between starch and PCLPU weakened alongside the physical cross-linking between PCL and PCLPU, creating a greater phase separation between starch and PCL in the composite material. The mechanical properties also exhibited a decreasing trend.

Scheme 1 was formed based on the above comprehensive analysis. The schematic diagram in Scheme 1(a) shows that the starch and PCL matrices were connected by very weak

interactions with hydrogen bonds. After adding PCLPU [Scheme 1(b)], the NCO groups of PCLPU and hydroxyl groups of starch formed strong urethane bonds. The PCLPU soft segments also played a role in establishing physical compatibility with the PCL matrix. Results showed that with increasing molecular weight of PCLPU soft segment [Scheme 1(b,c)], the interaction between PCLPU and PCL decreased. This occurred because soft segments with high molecular weight exhibited lower activity. Additionally, soft segments with higher molecular weight resulted in fewer interactions between the PCL matrix and the soft segment molecular chain per unit mass. Furthermore, with any increase in the molecular weight of the PCLPU soft segments, the NCO content of PCLPU in the samples was reduced, thus reducing the number of urethane bonds, resulting in a decreased interaction between PCLPU and starch.

CONCLUSIONS

In this study, PCLPU was synthesized by varying soft segments molecular weights to prepared starch-PCLPU-PCL composites. Compared with starch-PCL composites without any addition of PCLPU, the compatibility between starch and PCL increased significantly in the composites after adding PCLPU. XRD, mechanical properties testing, DSC, DMA, and SEM results showed that with decreasing molecular weight of PCLPU soft segments, the compatibility between starch and PCL improved significantly. This was facilitated by the greater reaction of NCO groups with starch hydroxyl groups allowed by PCLPU soft segments with low molecular weight, plus the stronger interaction with PCL matrices by physical cross-linking. Also, after the addition of low molecular weight PCLPU soft segment, the crystallinity of starch-PCLPU-PCL composites decreased, and the melting temperature increased. In conclusion, this study proved that, the addition of low molecular weight PCLPU soft segment successfully enhanced the properties of starch-PCL composites.

ACKNOWLEDGMENTS

This research was supported by Wuhan Public Relations Project of Science and Technology (2015060202010119).

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