

Effect of Reactive Blocked Polyisocyanate on the Properties of Solvent Cast Blends from Poly(lactic acid) and Poly(ethylene glycol)

Tengfei Shen,^{1,2} Mangeng Lu,¹ Dewen Zhou,^{1,2} Liyan Liang¹

¹Guangzhou Institute of Chemistry, Chinese Academy of Sciences, Guangzhou 510650, People's Republic of China

²Graduate School of the Chinese Academy of Sciences, Beijing 100049, People's Republic of China

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ABSTRACT: Poly(lactic acid) (PLA)/poly(ethylene glycol) (PEG) blends containing reactive ethyl cellosolve-blocked polyisocyanate (EC-bp) as a crosslinking agent with the goal of making sustainable “eco-friendly materials” were prepared using solvent casting method. Effects of such crosslinking agent and PEG additive on the properties of the prepared blends were investigated and compared. The morphology of the blends, evaluated by environmental scanning electron microscopy (ESEM), indicated that improved interfacial adhesion between PLA and PEG were achieved by the crosslinking effect of EC-bp. Tensile properties and water resistance were also studied and the results showed that these properties of EC-bp modified blends were signifi-

cantly enhanced in comparison with the unmodified ones. Differential scanning calorimetry (DSC) and X-ray diffraction (XRD) results showed that the degree of crystallinity (χ_c) of the blends was enhanced in the presence of PEG domains, whereas crystallization rate was decreased by addition of EC-bp. Dynamical mechanical analysis (DMA) showed that enhanced storage modulus and heat resistance of the blends were obtained when EC-bp was introduced as a crosslinking agent. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 125: 2071–2077, 2012

Key words: blends; morphology; mechanical properties; thermal properties; blocked polyisocyanate

INTRODUCTION

Since the serious environmental problem caused by nondegradable petroleum-based plastic products, the development of biomaterials from biodegradable polymers has attracted growing worldwide interest in the composite science because of their degradable, renewable, and eco-friendly properties.^{1–3} Biodegradable polymers have been the new subject of research and development in many studies during the last few years.^{4–6}

Among the biodegradable polymers, PLA has attracted great attention as a candidate for us in practical applications since it has a great potential to replace petroleum-based plastics. Moreover, PLA has proven to be the most attractive biodegradable polyesters because of their excellent biodegradability, biocompatibility, and bioresorbability.^{7,8} PLA is a commercially available biopolymer produced from

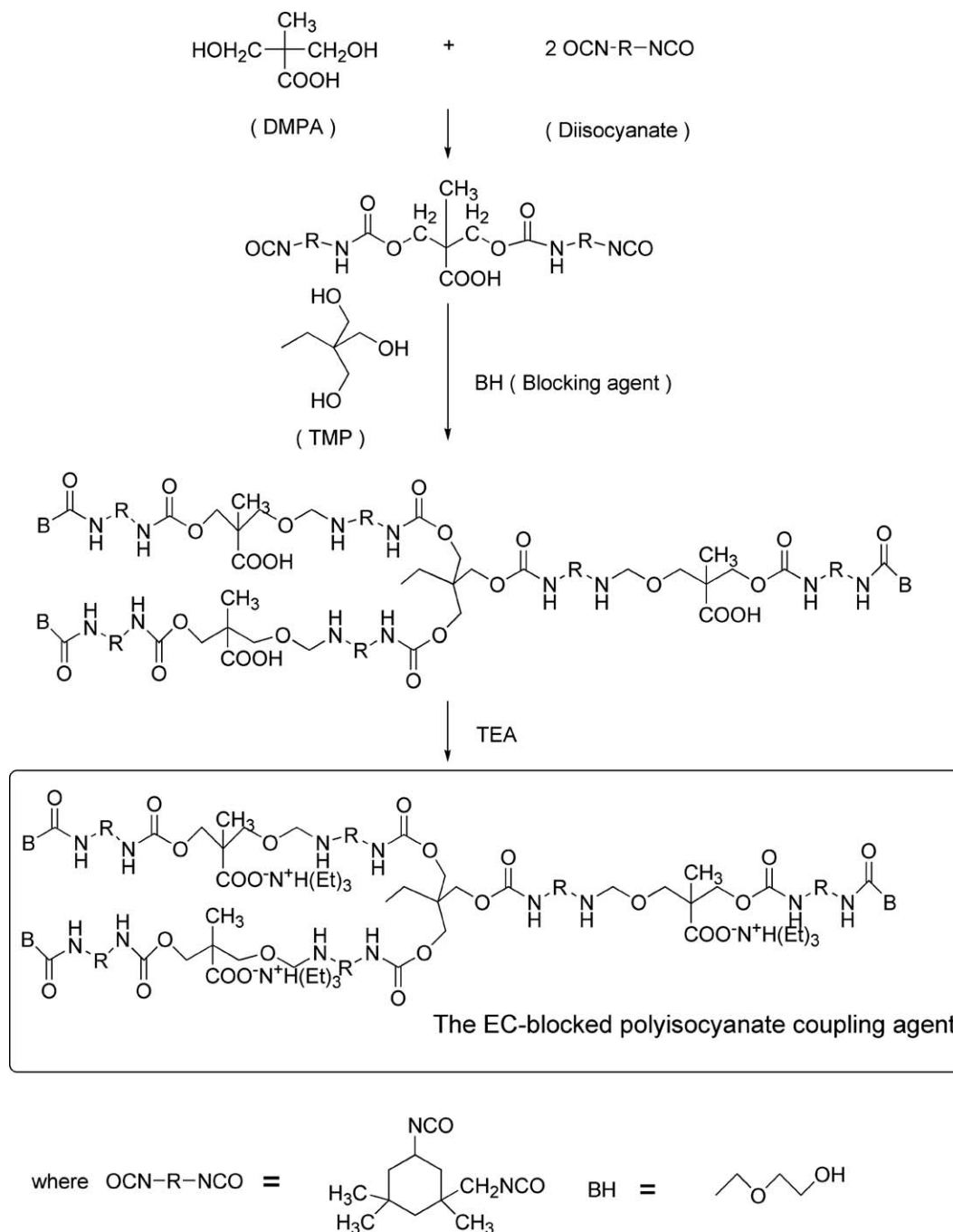
lactid acid, which typically comes from the fermentation of corn starch,^{9,10} which is suitable for the development trend of eco-friendly materials for now. Recently, PLA is widely used as a versatile polymer with applications in the medical, textile, and packaging materials fields.^{11–15} However, the elevated price and the brittle character limit the practical applications.

To overcome the drawbacks of PLA mentioned above, PEG is used to prepare PLA/PEG blends using solvent casting method in this work. PLA/PEG blends have attracted great interest as a new kind of biomaterials for their good biocompatibility and biodegradability.¹⁶ However, they also suffer from poor mechanical and thermal properties because of the weak interfacial adhesion. In recent years, it is widely reported that well-defined copolymer could act as emulsifying agent in immiscible polymer blends.^{17,18} These reported modified blend materials have enhanced mechanical properties, but almost all the blending were accompanied by a significantly drop in the modulus and heat resistance.

The chemistry of the urethane bond, based on the reaction of isocyanates with alcohols, has been largely investigated. Different studies have demonstrated the reversibility of the urethane bond and its thermal dissociation.¹⁹ In fact, the instability of these

Correspondence to: M. Lu (mglu@gic.ac.cn).

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Scheme 1 Synthetic route and the structure of EC-blocked polyisocyanate.

linkages at high temperature is of great concern. Under these conditions, the released isocyanate groups remain highly reactive toward most common functional groups, as indicated by the many molecular rearrangements that take place in the processed thermoplastic polyurethane.²⁰ The rate and extent of deblocking reaction depend on many factors: the structure of isocyanate and blocking agent including substituents, solvents, catalysts, temperature, and the thermal stability of the isocyanate-blocking agent bond.^{21,22}

Considering the above reasons, synthesized reactive ethyl cellosolve-blocked polyisocyanate was used as a novel crosslinking agent in our work. Recently, we reported that such blocked polyisocyanate could maximum thermally deblock in the temperature around 150°C,²³ which is good for the manufacturing process. In this work, the effect of such crosslinking agent on the properties of the prepared PLA/PEG blends was investigated and discussed. The results showed that not only the mechanical and interfacial properties, but also the

TABLE I
Prepared Composite Formulations

Composites	Composition (w/w)	EC-bp added (wt %)	Code
PLA/PEG	100/0	–	PLA
PLA/PEG	90/10	–	P1
PLA/PEG	80/20	–	P2
PLA/PEG	70/30	–	P3
PLA/PEG	90/10	0.5	P1-EC-0.5
PLA/PEG	90/10	1	P1-EC-1
PLA/PEG	90/10	2	P1-EC-2

modulus and the heat resistance were significantly improved by addition of such novel reactive ethyl cellosolve-blocked polyisocyanate because of its good crosslinking effect.

EXPERIMENTAL

Materials

PLA ($M_w = 170,000$ g/mol; $M_n = 100,000$ g/mol) was purchased from Cargill-Dow; PEG ($M_n = 20,000$ g/mol) was supplied by Kanto Chem. Co. PLA and PEG were vacuum-dried at 40°C and 100°C for 48 h prior to use, respectively. EC-bp was synthesized in our laboratory. The synthetic route and its structure are presented in Scheme 1. All other chemicals were purchased from commercial sources.

Blends preparation

PLA, PEG, and 0.5–2 wt % EC-bp were dissolved in dry cosolvent of chloroform and ethanol ($V/V = 5 : 1$) to form 10 wt % homogeneous solution by stirring the solution on a water bath at 60°C for 3 h. Subsequently, the blending was cast onto Teflon mould to generate film after solution evaporation at room temperature, followed by vacuum drying until the mass of the film became constant. The samples were baked at 150°C for 0.5 h for the crosslinking reaction. The formulations are given in Table I.

Environmental scanning electron microscopy

Environmental scanning electron microscopy (ESEM; Quanta 400 FEI) was used to evaluate the fracture surfaces and interfacial adhesion of the prepared blends. The accelerating voltage applied was 20.0 kV. The fracture surfaces of samples for ESEM were generated by cryofracture under liquid nitrogen.

Tensile testing

Tensile properties of the blends were measured using a universal materials testing machine 3030 (INSTRON) at a crosshead speed of 10 mm/min.

Sample specimens were prepared with a die of dimensions of 8 mm width, 50 mm length, and 1.0 mm thickness, the grip distance was set at 25 mm. All test results presented are the average values of five measurements.

Water absorption

Water absorption test: Preweighed dry samples were immersed in deionized water for 4 weeks to study water absorption at room temperature. After immersing, the samples were blotted with a laboratory tissue and weighed, immediately weighted to the nearest 0.001 g. The final water absorption was expressed as the weight percentage of water in the swollen sample:

$$\text{Water absorption (\%)} = (W_W - W_D)/W_D \times 100\%,$$

where W_D is weight of the dry sample and W_W is the weight of the swollen sample.

Differential scanning calorimetry

Differential scanning calorimetry (DSC) measurements were performed on a DSC Q200 (TA instruments, USA) in the temperature range of 0°C–200°C using ~ 8 mg of samples. The samples were tested at nonisothermal conditions at the same heating and cooling rates of 10°C/min.

X-ray diffraction

The X-ray diffraction (XRD) patterns were obtained from radiation generated by the copper target of a Rigaku Diffractometer (D/MAX-1200) set at 40 kV and 20 mA, with the detector placed on a goniometer scanning from 5° to 60°.

Dynamical mechanical analysis (DMA)

Storage modulus and loss factor ($\tan \delta$) of the blends were measured as a function of temperature (0°C–150°C) using a TA 2980 DMA equipped with a dual-cantilever bending fixture at a frequency of 1 Hz and a heating rate of 5°C/min.

RESULTS AND DISCUSSION

Morphology analysis

It is well known that many properties of blend materials can be affected by the properties of the individual blend components and their interfacial interactions. Therefore, controlling of the morphology of the blends is a key factor for the tailoring of the final properties of the blend materials.^{17,24}

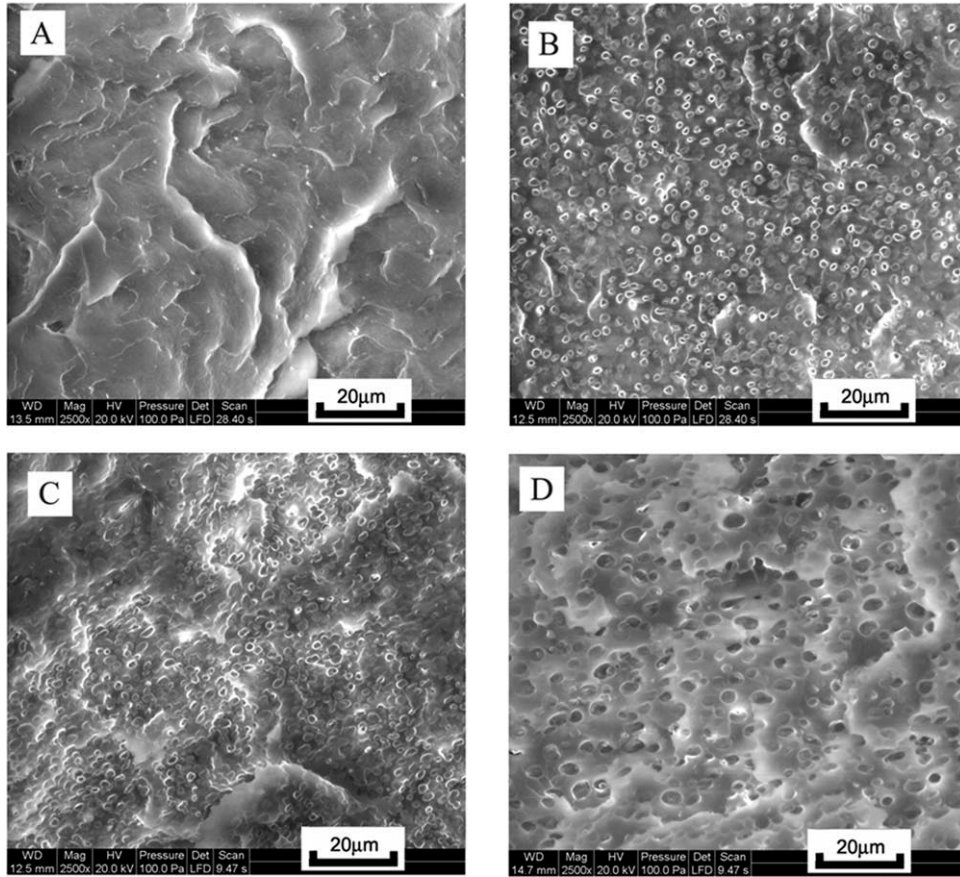


Figure 1 ESEM micrographs of cryofratured surfaces of neat PLA and PLA/PEG blend at 2500× magnification (A) PLA; (B) P1; (C) P2; (D) P3.

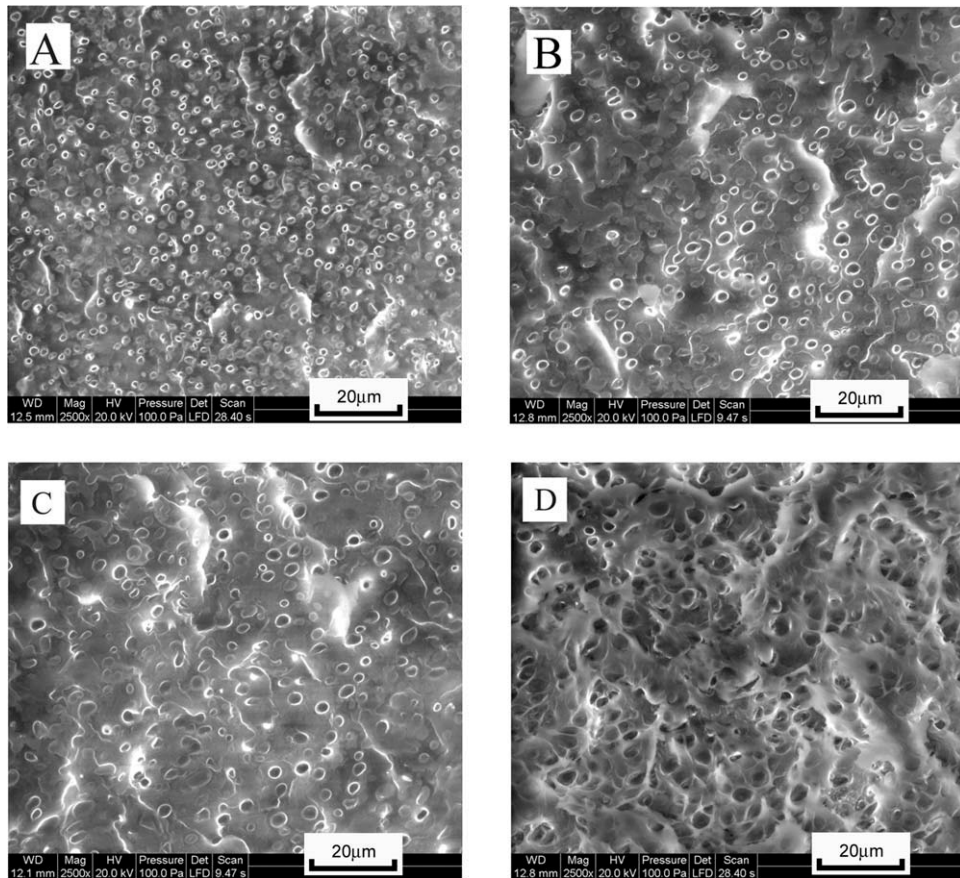


Figure 2 ESEM micrographs of cryofratured surfaces of of PLA/PEG blend at 2500× magnification (A) P1; (B) P1-EC-0.5; (C) P1-EC-1; (D) P1-EC-2.

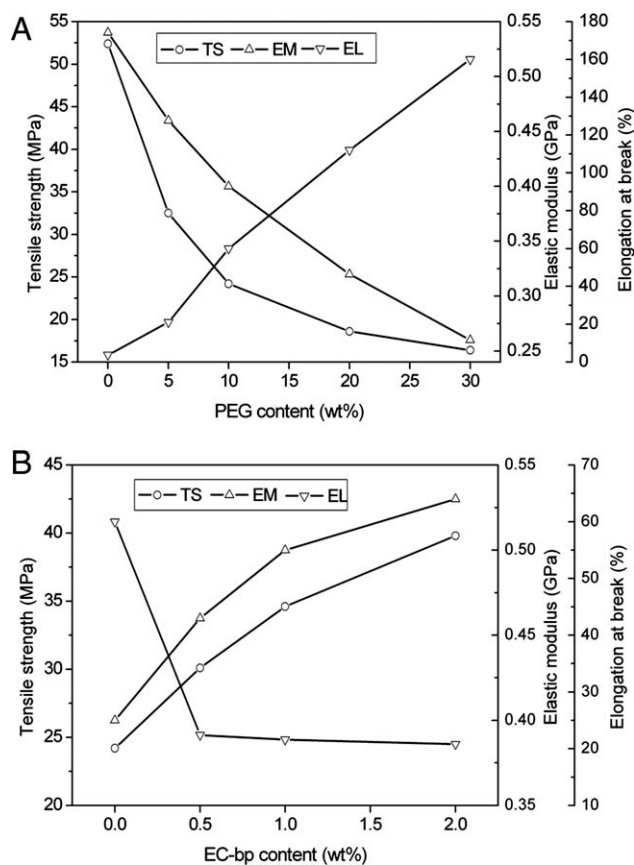


Figure 3 Effects of (A) PEG content and (B) EC-bp content on the tensile properties of the blends.

Figure 1 showed the ESEM micrographs of cryo-fractured surfaces of neat PLA and unmodified PLA/PEG blends. They indicated fine blend morphologies with dispersed phase (PEG) domains, which are spherical in shape. The sphere size increased as PEG concentration increased because of coalescence phenomena. It is widely reported that PEG has spherical structure.^{25–29} In addition, sharp interface between polymer matrix (PLA) and disperse phase (PEG) were visible, which indicated poor interfacial adhesion of the unmodified blends.

Figure 2 showed the ESEM micrographs of cryo-fractured surfaces of EC-bp modified PLA/PEG blends. It was found that the interface between PLA and PEG appeared to be indiscernible, caused by the crosslinking effect of the addition of EC-bp in comparison with unmodified one, which indicated that better interfacial adhesion was achieved by addition of EC-bp. This phenomenon was more evident as EC-bp content increased.

Tensile properties

Tensile properties of PLA/PEG blends with and without EC-bp are shown in Figure 3. It could be

seen that blends with EC-bp showed higher values than the blend without because of the strong chemical reaction of released NCO groups from EC-bp and OH groups from PEG and PLA imparted by the crosslinking agent. Figure 3(A) showed the effect of PEG content on the tensile properties of the blends. It was found that the tensile strength (TS) and elastic modulus (EM) gradually decreased as PEG content increased, whereas the elongation at break (EL) increased steeply. Comparing P1 with P3 blend, elongation at break value increased from about 60% to 160%, elastic modulus decreased from 400 to 260 MPa, and tensile strength decreased from 24.2 to 16.4 MPa. This was because of the strong flexible properties of PEG.

Effect of EC-bp content on the tensile properties of the blends is shown in Figure 3(B). It was observed that tensile strength and elastic modulus increased with increasing EC-bp content, whereas the elongation at break decreased. In the case of P1 blend, as EC-bp content increased to 1 wt %, elastic modulus and tensile strength increased from 400 to 500 MPa and from 24.2 to 34.6 MPa, respectively. This was because of the crosslinking between PLA and PEG by addition of EC-bp. The intense reaction between the released isocyanate groups with hydroxyl or carboxyl groups has been reported.^{30,31}

Water absorption

Effects of EC-bp and PEG content on the water absorption of the blends were investigated and are depicted in Figure 4. It could be seen that the EC-bp modified blends exhibited much better water resistance than the unmodified one. In the case of P1 blend, it showed almost sevenfold increase percent swelling in water compared with P1-EC-1 in four weeks. This indicated that the addition of EC-bp

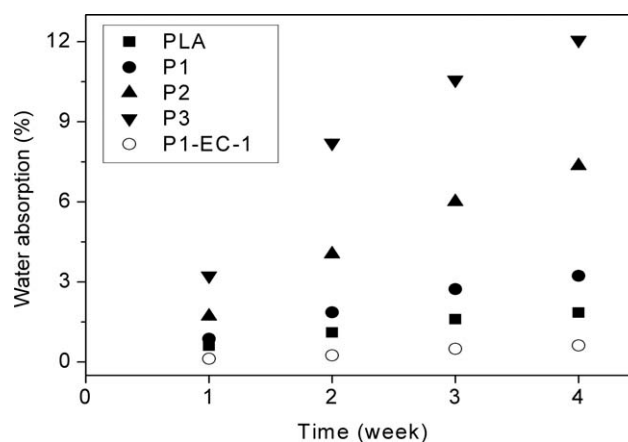


Figure 4 Effects of the addition of EC-bp and PEG content on the water absorption behavior of PLA/PEG blends.

indeed limited the absorption of water, which could be explained by the improvement on interfacial adhesion because of the reaction of released NCO groups with OH groups from PLA and PEG. In addition, we observed that neat PLA absorbed only about 2 wt% water in 4 weeks, but around 12 wt% for P3 blend. The water absorption increased rapidly with increasing PEG content because of the strong hydrophilic of PEG.

Crystallization and thermal behaviors

X-ray diffraction patterns of neat PLA and PLA/PEG blends with and without EC-bp are shown in Figure 5. Based on the X-ray patterns, we could confirm that the samples of neat PLA and its blends were semicrystalline. In the crystallized state, PLA and its blends (P1 and P1-EC-1) showed crystalline peaks at around $2\theta = 16^\circ$ and 19° , in agreement with previous papers.^{32,33} Consequently, the degree of crystallinity (χ_c) of the blends could be obtained by this technique. The detail data were given in Table II.

DSC was carried out to investigate the thermal properties of the blends. Glass transition temperature (T_g), crystallization temperature (T_c), melting temperature (T_m) of neat PLA and its blends were determined and the obtained results are summarized in Table II. It can be found that both T_g and T_c shifted to lower temperature as PEG content increased. This was consistent with the fact that PLA crystallizes more easily at lower temperature because of the enhanced molecular chain motion as PEG content increased.

On the contrary, T_g and T_c shifted to higher temperature by addition of EC-bp, and increased as its concentration increased. This should be because of

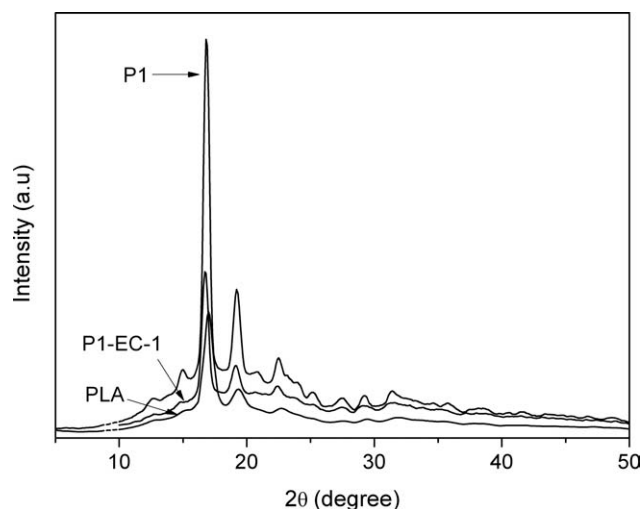


Figure 5 X-ray diffraction patterns of neat PLA, P1, and P1-EC-1.

TABLE II
Crystallization and Thermal Behavior of the Neat PLA and Its Composites with and Without EC-bp

Samples	T_g ($^\circ\text{C}$)	T_c ($^\circ\text{C}$)	T_m ($^\circ\text{C}$)	χ_c (%)
Neat PLA	59.5	126.8	149.2	35.20
P1	39.4	98.1	143.0–150.3	42.18
P2	23.1	82.0	141.8–150.3	45.29
P3	14.6	75.2	140.1–150.3	51.50
P1-EC-0.5	42.2	101.1	143.5–150.5	38.71
P1-EC-1	46.1	105.2	144.6–151.7	35.02
P1-EC-2	56.6	117.7	148.2	30.18

the crosslinking reaction between PLA and PCL induced by EC-bp. The degree of crystallinity (χ_c) of the modified blends decreased because the existed EC-bp diminished the molecular chain motion, resulting in the slow crystallization rate.

Thermomechanical properties

To study the effects of the addition of PEG and EC-bp on the thermomechanical properties of the blends, we performed DMA measurement on the prepared samples. The temperature curves of storage modulus and loss factor for neat PLA and its blends are shown in Figure 6.

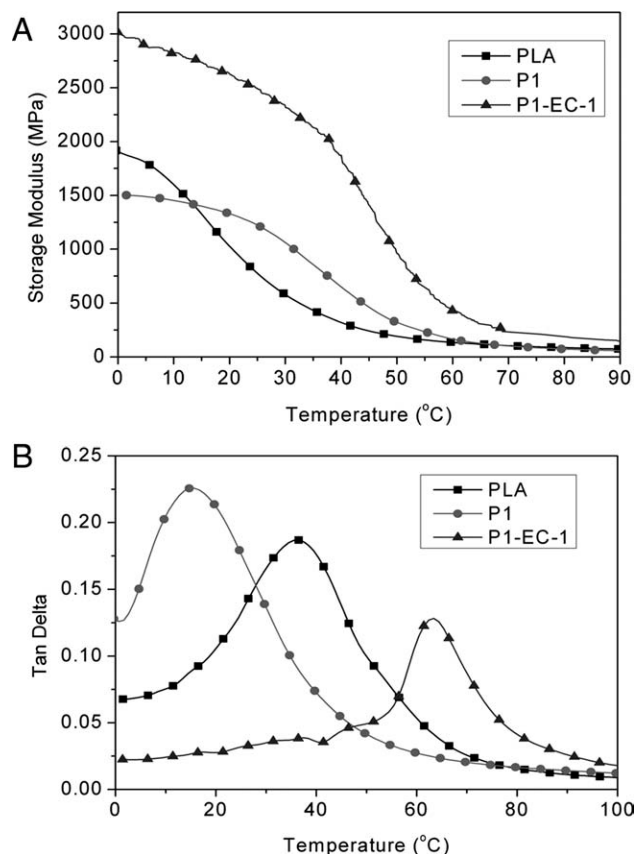


Figure 6 Storage modulus curves (A) and $\tan \delta$ peaks (B) from DMA of PLA, P1, and P1-EC-1.

As seen from Figure 6(A), it was found that the storage modulus of the unmodified PLA/PEG blend was lower than neat PLA. Comparing P1 with neat PLA, the storage modulus decreased from 1.9 to 1.5 GPa. In the meantime, we observed that the storage modulus was enhanced obviously by addition of EC-bp. Storage modulus increased from 1.5 to 3 GPa when comparing P1-EC-1 with P1. In addition, it revealed that the EC-bp modified blend (P1-EC-1) showed longer plateau on the storage modulus than neat PLA and the unmodified blend (P1), which indicated that an improvement on thermal stability of the blend by addition of EC-bp.

Figure 6(B) showed the loss factor ($\tan\delta$) of PLA and its blends as a function of temperature, where the ratio of storage modulus and loss modulus gives the tangent of the phase angle delta, a measurement of energy dissipation. The T_g is usually interpreted as the peak of the $\tan\delta$ obtained during dynamic mechanical analysis. It was found that the T_g of the EC-bp modified blend (P1-EC-1) shifted to higher temperature. The shifting of T_g to higher temperature was associated with the decreased mobility of the molecular chain, which suggested that enhanced interfacial adhesion between PLA and PEG was achieved because of the crosslinking effect of EC-bp.

CONCLUSIONS

In this work, PLA/PEG blends were successfully prepared by solvent casting method. Ethyl cello-solve-blocked polyisocyanate (EC-bp) as a novel crosslinking agent was introduced to improve the mechanical and thermal properties of the blends. The results showed that tensile properties and water resistance were obviously enhanced by the addition of such crosslinking agents. ESEM showed that improved interfacial adhesion of the blends was achieved when EC-bp was added. The crystallization and thermal properties of the blends were studied and compared by XRD and DSC techniques. The degree of crystallinity of PLA was enhanced in the presence of PEG additive, whereas the crystallization rate was decreased by addition of EC-bp. DMA showed that the storage modulus and heat stability of EC-bp modified blends were enhanced in comparison with the unmodified one. Furthermore, all testing results suggested that EC-bp could be as a

potential crosslinking agent in many application areas of biomaterials.

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