Mechanical and Thermal Properties of Toughened Poly(L-lactic) Acid and Lignin Blends

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Fully degradable poly(L-lactic) acid (PLLA) and lignin blends were prepared using the melt blending method. The impact strength of PLLA was dramatically improved by 52.4% and 36.6% with the addition of 5 wt% and 10 wt% of lignin, respectively. Meanwhile, the Young's modulus was maintained. Polarized optical microscopy (POM) results indicated that lignin served as a nucleating agent for the heterogeneous crystallization of PLLA in blends, which was responsible for the improvement in the impact strength. The introduced lignin also promoted the cold-crystallization of PLLA, which was demonstrated by differential scanning calorimetry (DSC). The blends of PLLA with lignin are considered to be a promising material because of the improved toughness, the full degradability, and the lower price compared with pure PLLA.

Keywords: Poly(L-lactic) acid; Lignin; Toughening; Heterogeneous nucleation; Fully degradable blends

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INTRODUCTION

Lignin is a network polymer consisting of phenyl propane units (-C_6-C_3-), in which the characteristic aromatic rings are substituted by one methoxyl group, two methoxyl groups, or no methoxyl groups (Abdul Khalil *et al*. 2011; Li *et al*. 2011; Pucciariello *et al*. 2004; Santos *et al*. 2013; Zhang *et al*. 2013). Lignin is one of the most abundant non-toxic, amorphous, natural biopolymers, second only to cellulose (Lundquist and Parkas 2011; Oliviero *et al*. 2011; Sahoo *et al*. 2011). It serves as a continuous matrix component in plant cell walls, providing mechanical strength and structural support (Ibrahim *et al*. 2011; Rozman *et al*. 2011; Silva *et al*. 2011; Yue *et al*. 2011, 2012). However, almost 99% of lignin is either burned in an energy recovery step in the pulping process or disposed of in waste streams (El-Wakil 2009; Song *et al*. 2011; Yuan *et al*. 2011). This not only produces large amounts of carbon dioxide polluting the environment, but also wastes resources. Extrapolating just 1% of these renewable raw materials would cause a revolution in environmental protection and energy.

Currently, due to the rapid decrease of petroleum energy sources and environmental pollution coming from petroleum-derived plastics, biodegradable and bio-based polymers have received extensive interest as an alternative to conventional petroleum-based plastics (Tawakkal *et al*. 2012; Zhang *et al*. 2013; Zhang *et al*. 2012). Among the degradable polymers, only a few aliphatic polymers, such as poly(lactic acid) (PLA), poly(ε-caprolactone)(PCL), poly[(butylenesuccinate)-*co*-(butylene adipate)], and polyhydroxyalkanoates, are now commercially available around the world (Li *et al*. 2003). Compared with other such kinds of materials, PLA shows better tensile strength and processing properties and is the most promising bio-based polymer commercially available in the market (Li *et al*. 2003). Commercial PLA is synthesized by ring-opening polymerization of lactides, which are the cyclic dimer of lactic acids and are typically derived from renewable resources such as corn, sugar beets, and rice (Yao 2011). In addition, poly(lactic acid) is nontoxic to the human body and the environment (Chen *et al*. 2013), degradable, easy to fabricate, and has a high degree of transparency (Rangari and Vasanthan 2012). However, because of its defects, such as poor toughness, low glass transition temperature (ranging from 55 to 65 °C), low and uncontrollable biodegradation rate, and relatively high price, PLA-based products have not became popular in consumer markets (Dorati *et al*. 2007; Yeh *et al.* 2008).

In this study, the system of interest involves the combination of PLLA (poly(L-lactic) acid) and lignin to produce fully degradable polymer blends. Lignin is considered a promising filler or additive to be used in polymers because of its low price, low density, low abrasive character, good thermal stability, and high reactivity (Maldhure *et al*. 2012; Rosu *et al*. 2009; Sevastyanovav *et al*. 2010; Song *et al*. 2011; Wood *et al*. 2011). These advantages make it far more attractive than other organic or inorganic fillers. Incorporation of lignin in poly(L-lactic) acid helps to lower the cost of the finished product as well as to give some biodegradable characteristics to the thermoplastic polymers. In addition, the excellent thermal and photo stability of lignin may provide a synergistic effect with the properties of poly(L-lactic) acid.

Recently, there have been a few papers focused on PLLA/lignin blends, but properties such as tensile strength and impact strength are reduced to some extent (Li *et al*. 2003; Ouyang *et al*. 2011). As far as we know, there are no reports that lignin contributes to the improvement of the toughness of PLLA. In this work, PLLA/lignin blends prepared by the extrusion method and the effects of lignin on the mechanical and thermal properties of the PLLA/lignin blends were investigated.

EXPERIMENTAL

Materials

Poly(L-lactic) acid, 2003D, having a D-isomer molar content of 4.3%, was purchased from NatureWorks, USA. Lignin powder (pH of 5.35, ash content of 1.24% and electrical conductivity of 200 µS/cm), derived from cornstalk under high pressure and not water-solubility, was kindly supplied by Shandong Shengquan group Co. Lt. Lignin was ground with a high-speed universal grinder (FW-400A, 26000 r/min) into powder into powder and sieved with a sieve of 60 meshes before use.

Methods

Preparation of PLLA/lignin blends

PLLA granules and lignin powders were dried in a convection oven at 80 ^{o}C for 12 h. Dried materials were weighted separately according to the proportion and placed in a plastic bag for thoroughly manual mixing. The mixture was subsequently fed into a twin-screw SHJ-30-China extruder (China, slenderness ratios of 40 (L/D)) at a screw speed of 90 rpm and at the temperatures of 120-135-155-163-163-163-158 ^{o}C from hopper to die. The strands of the extrudate were chopped into pellets and collected. The pelletized blends were then dried at 80 °C for 12 h and injected by a NISSEI-PS40E5A5E injection-molding machine (Nissei Corporation, Japan) at temperatures of

160-170-165 °C, injection pressure of 5-50 MPa, and with a cooling time of 40 s. Finally, the coupons were aged 48 h at room temperature before mechanical test.

Measurements

Tensile properties were measured according to ASTM D 638 (1999) using a Shimadzu AGS-J tensile testing machine (Japan) with the speed of 50 mm/min. Notched Izod impact strength was measured with an XC-22Z impact tester (Chengdu, China) according to ASTM D 256-04. All the measurements were carried out at room temperature (23 ± 2 °C). At least six replicates were tested, and the average values are reported.

The fracture surfaces after tensile tests and freeze-fractured specimens that were cryogenically frozen with liquid nitrogen for 1 h were examined using a scanning electron microscope (SEM) (FEI Inspect, Philips, the Netherlands) with an accelerating voltage of 5.0 kV. The morphology of lignin is also characterized by SEM observations. Prior to examination, the samples were sputtered with gold using JEOL Fine Coater JFC-1200 for 50 s at argon pressure of 8 Pa and current of 30 mA.

The particle distribution of original lignin were measured by laser particle analyzer (SJ-6000, Chengdu, China). Samples were dried at 80 °C for 12 h before laser particle analysis.

An optical microscope with polarized optics (POM, XPN-203, China) consisting of one hot-stage was used to characterize the isothermal crystallization morphologies of PLLA/lignin. A sample of about 5 mg was placed between two glass slides on the hot-stage (at 190 °C) and was heated to melt completely. After pressing into a slice with a thickness of about 20 µm, the sample was cooled down to 105 °C at a cooling rate of 20 °C/min and maintained at this temperature for 1 h on the hot-stage. The crystallization morphologies of the samples were studied *via* images taken with a digital camera.

Differential scanning calorimetry (DSC) measurements were performed on a DSC (Netzsch STA449C Jupiter; Germany) with nitrogen purge at a flow rate of 100 mL/min. The instrument was calibrated for temperature and enthalpy by high purity indium (156.60 °C, 28.45 J/g) standard. Every blend sample (8 ± 2 mg) was heated from 0 to 210 °C at a scanning rate of 10 °C /min in a nitrogen atmosphere.

RESULTS AND DISCUSSION

Mechanical Properties

The mechanical properties of PLLA/lignin blends are shown in Table 1. Compared with neat PLLA, PLLA/lignin blends with 5 wt% lignin yielded a marked improvement in impact strength (52.4%) and elongation at break (97.1%). When 10 wt% lignin was added to PLLA, the impact strength and elongation at break decreased marginally, but were still higher than neat PLLA. The Young’s modulus of the blends was not decreased before the lignin fraction reached 10 wt%. Table 1 also showed that the tensile strength decreased with increasing lignin content in the blends.

According to the data shown in Table 1, the tensile strength decreased from 64.9 MPa for neat PLLA to 43.3 MPa for the blends with 20 wt% lignin, a decrease of 33%, higher than the 24% calculated by Ouyang *et al*. (2011), but much lower than the 58% reported by Li *et al*. (2003). Conversely, the impact strength and elongation at break increased with a suitable amount of lignin (5 wt% or 10 wt%) in our work, while it always deceased in the study by Ouyang *et al*. (2011). The elongation at break was also decreased in the report by Li *et al*. (2003). Clearly, the addition of lignin improved both the ductility and toughness of PLLA to some degree in the present work.

Table 1. Mechanical Properties of the PLLA/Lignin Blends

Lignin Content *****	Impact strength (KJ/m^2)	Elongation at break (%)	Young's modulus (MPa)	Tensile strength (MPa)
0 wt%	8.2 ± 0.1	10.3 ± 0.4	1578 ± 15	64.9 ± 0.3
5 wt%	12.5 ± 0.5	20.3 ± 0.5	1589 ± 10	55.1 ± 0.2
10 wt%	11.2 ± 0.1	17.9 ± 0.5	1586 ± 3	48.6 ± 0.4
20 wt%	7.1 ± 0.6	8.0 ± 0.5	1543 ± 19	43.3 ± 0.3
30 wt%	6.3 ± 0.4	5.0 ± 0.2	1562 ± 4	38.0 ± 0.1
***** based on weight of the blends				

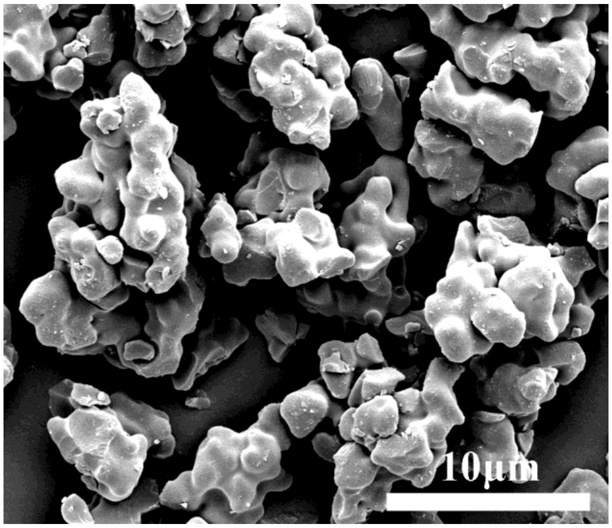

Fig. 1. SEM photograph for the morphology of lignin

Table 2. Particle Size and Distribution of Lignin

Sample	D50	D[4,3]	D3	D97	Surface area/Volume *****
Lignin	2.164	4.409	0.241	15.973	4.847
***** the unit of it is m^2/cm^3 and the others μm					

The SEM micrograph, as shown in Fig. 1, reveals the spherical morphology of lignin. Many agglomerates and some spherical particles can be seen, and it is difficult to determine the primary size of lignin precisely due to aggregation of lignin. The particle size and distribution of lignin were precisely evaluated by laser particle analyzer, and the results are shown in Table 2.

It is well known that the filler size and its dispersion in the polymer matrix as well as the interfacial interactions between filler and matrix will show a great effect on the mechanical properties of polymer blends. In this work, lignin was seen to be well-dispersed in PLLA matrix even at a high lignin content of 30 wt% and homogeneous dispersion of lignin in PLLA was achieved as shown in Fig. 2. Furthermore, the dispersion size of lignin in Fig. 2 was much smaller than that in Fig. 1. It was obvious that the sharp drop in tensile strength of PLLA/lignin composites compared to neat PLLA was not caused by the poor dispersivity of lignin in PLLA matrix.

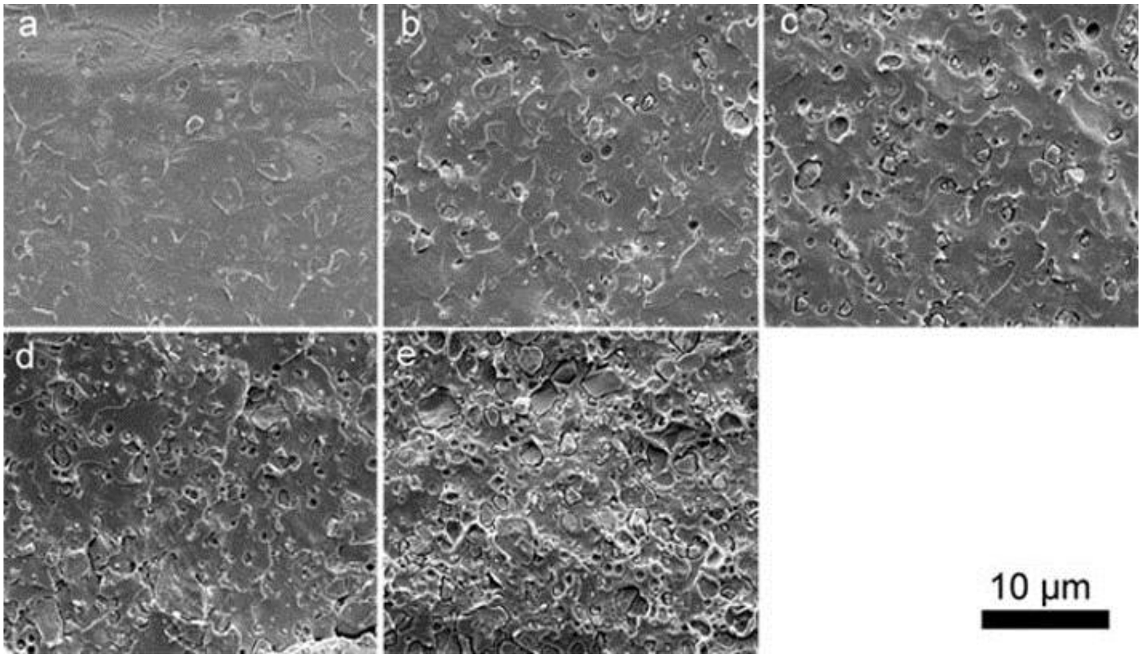

Fig. 2. SEM micrographs of freeze-fractured surfaces of PLLA/lignin blends with different lignin contents: (a) 0 wt%; (b) 5 wt%; (c) 10 wt%; (d) 20 wt%; and (e) 30 wt%

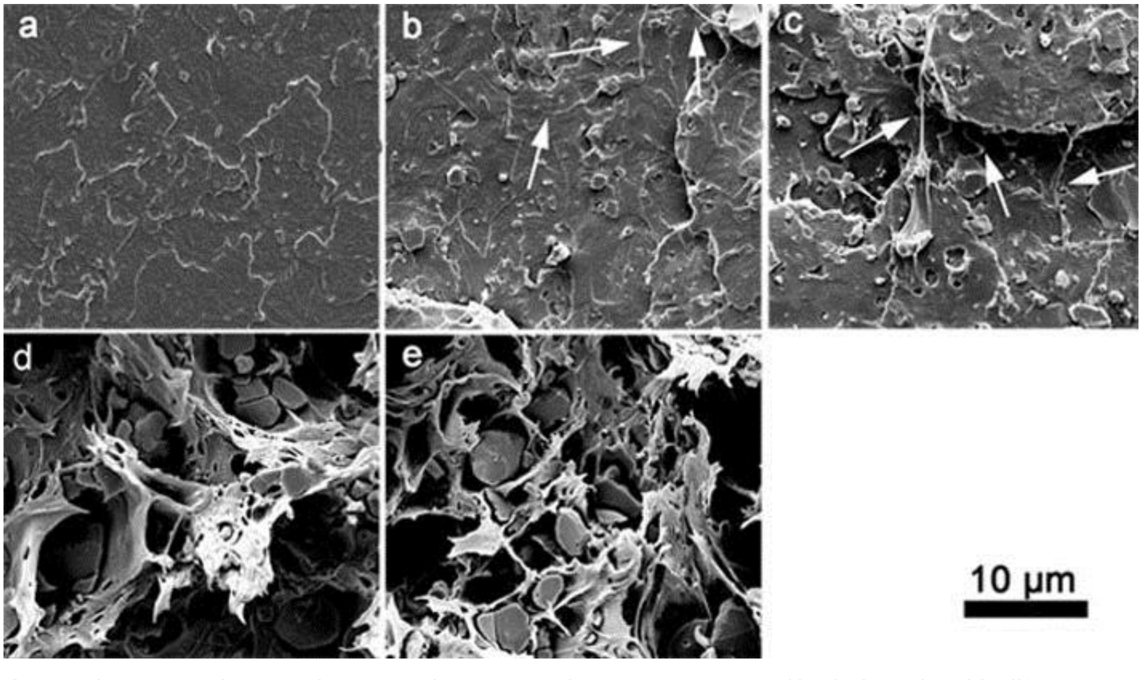

Fig. 3. The SEM micrographs of tensile-fractured surfaces of PLLA/lignin blends with different lignin contents: (a) 0 wt%; (b) 5 wt%; (c) 10 wt%; (d) 20 wt%; and (e) 30 wt%

Figure 3 shows SEM micrographs for tensile-fractured surfaces of PLLA/lignin blends. It can be seen that all the samples were fragile materials, while the PLLA/lignin blends samples with 5 wt% and 10 wt% lignin exhibited some toughness. In the PLLA/lignin blends samples with 5 wt% and 10 wt% lignin, there was a small number of fibrils (shown by the arrows in Fig. 3b and Fig. 3c). This suggested that the blends were able to withstand the load at a low filler loading level. When the lignin loading increased to 20% and 30%, the tensile-fractured surfaces showed large holes between PLLA and lignin because of the poor miscibility of lignin in the PLLA matrix. Furthermore, the voids produced by lignin particles were all in close proximity to each other. Most of the stress were transferred by PLLA matrix, and it reflected a sharp decrease in the tensile strength. As for the improved ductility of PLLA/lignin blends with 5 wt% and 10 wt% lignin, maybe lignin with small size have acted as plasticizer and at last induced the improvement of the elongation at break.

To determine the toughening mechanism, polarized optical microscopy (POM) images were examined. Figure 3 shows the POM results for the PLLA/lignin blends. It was very difficult to differentiate the spherulites one by one in Figs. 3a to 3d. The number of spherulites in Figs. 3b to 3d was much higher than that in the neat PLLA (Fig. 4a), and the size was much smaller than that in the neat PLLA. Higher lignin content resulted in more and smaller spherulites. This provides support for the heterogeneous nucleation effect of lignin with PLLA. The heterogeneous nucleation effect resulting from addition of lignin may be the reason for the improved impact strength.

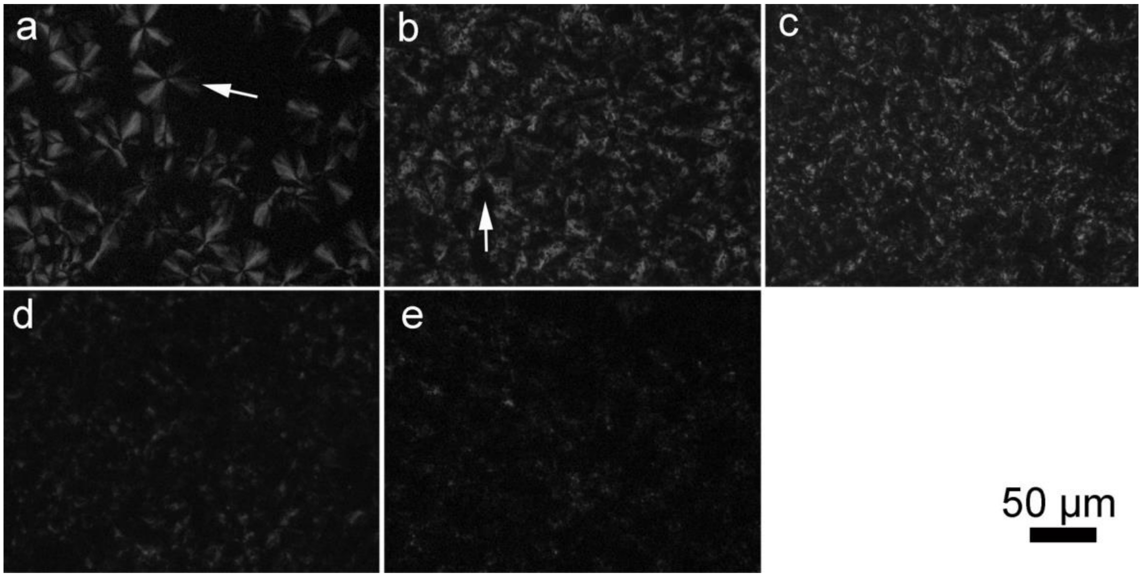

Fig. 4. The POM images of the crystal morphology for PLLA/lignin blends with different lignin contents: (a) 0 wt%; (b) 5 wt%; (c) 10 wt%; (d) 20 wt%; and (e) 30 wt%; Arrows in (a) and (b) denote representative spherulites

Thermal Properties

The DSC thermograms of PLLA/lignin blends are shown in Fig. 5, and the thermal characteristics were summarized in Table 3. Pure PLLA displayed a glass transition at 60.1 °C. The addition of lignin did not result in a noticeable change in the glass transition temperature. In Fig. 5, the blends yielded two melting peaks, T_{m1} and T_{m2}, although lignin had no melting temperature (Fig. 5f). It is widely accepted that the double endothermic peaks are attributed to the melting-recrystallization-melting process of PLLA lamellae: the melting peak T_{m1} originates from the fusion of thin lamellae (less perfect crystals) formed during the cooling process and T_{m2} comes from the fusion of newly formed lamellae (more perfect crystals) obtained through the melting-recrystallization process of thin lamellae (He *et al*. 2006; Wang *et al*. 2012). When a small amount of lignin (*e.g.*, 5 wt% or 10 wt%) was added to PLLA, the cold crystallization temperature shifted to a lower temperature (from the original 115 to 113 °C) (Table 3). This result indicated that lignin promoted the cold-crystallization of PLLA. For higher lignin contents (≥ 20 wt%), the segmental motion of PLLA molecular chains may have been affected by excess lignin; the crystallization capacity and the crystallization rate would then have been affected, leading to a shift in the cold-crystallization temperature to higher temperatures (from 113 to 116 °C and even to 121 °C). Furthermore, as the content of lignin increased, the intensity of the melting peak T_{m1} (Fig. 5) increased gradually, which indicated a gradually increasing amount of less perfect crystals; at the same time, the intensity of the melting peak T_{m2} (Fig. 5) decreased, indicating a gradually decreasing amount of more perfect crystals.

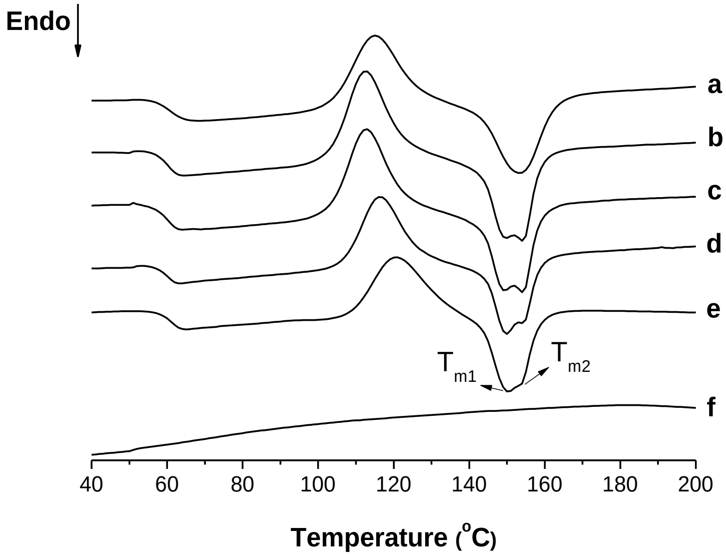

Fig. 5. The DSC heating curves of lignin and PLLA/lignin blends with different lignin contents: (a) 0 wt%; (b) 5 wt%; (c) 10 wt%; (d) 20 wt%; and (e) 30 wt%; and (f) lignin

Table 3. DSC Data for PLLA/Lignin Blends with Different Lignin Contents

Lignin Content *****	T_g (°C)	T_{cc} (°C)	T_m (°C)	
			T_{m1}	T_{m2}
0 wt%	60.1	115	—	155
5 wt%	60.2	113	150	154
10 wt%	59.9	113	150	154
20 wt%	60.3	116	150	154
30 wt%	61.0	121	150	154
***** based on weight of the blends				

CONCLUSIONS

1. The toughness of poly(L-lactic) acid was improved considerably (52.4%) by the addition of only 5 wt% lignin. With increasing lignin addition, the toughness of PLLA/lignin blends decreased to different extents, but the toughness of PLLA/lignin blends with 10 wt% lignin was still better than that of neat PLLA.
2. According to polarized optical microscopy (POM) results, lignin had a heterogeneous nucleation effect on PLLA/lignin blends, which resulted in the improved toughness of the PLLA/lignin blends.
3. Adding a small amount of lignin to PLLA can also promote the cold-crystallization of PLLA dramatically.
4. Compared with neat PLLA, blends of PLLA with lignin are considered a promising material because of their improved toughness, full degradability, and lower price compared with pure PLLA.

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