

멜트블론 부직포 제조를 위한 PLA/PCL 블렌드의 미세구조, 열적특성, 및 유변학적 성질

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Microstructure, Thermal Properties and Rheological Behavior of PLA/PCL Blends for Melt-blown Nonwovens

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Abstract: Poly(lactic acid) (PLA) and poly(ϵ -caprolactone) (PCL) blends with various components for melt-blown nonwovens were prepared by a twin-screw extruder. Tributyl citrate (TBC) was added in order to improve the miscibility between PLA and PCL. The results showed that small circular particles of PCL were dispersed in PLA matrix uniformly. The addition of PCL had the heterogeneous nucleation effect on the crystallization of PLA and decreased thermal stability of PLA. The flow of pure PLA and blends approached to Newtonian liquid at a low shear rate and expressed more obvious viscoelasticity at a high shear rate.

Keywords: poly(lactic acid), poly(ϵ -caprolactone), microstructure, thermal properties.

Introduction

In recent years, the massive use and disposal of petroleum-based plastics had been seriously caused public affairs over the environmental hazards. The main strategies to address these problems are to develop materials that are renewable, degradable, and recyclable, better known as "green materials," as alternatives to the petroleum-based materials.¹⁻⁴ The most popular and important biodegradable polymers are aliphatic polyesters such as polylactide (PLA), poly(ϵ -caprolactone) (PCL), polyethylene oxide (PEO), poly(ϵ -hydroxybutyrate) (PHB), and polyglycolic acid.^{5,6}

The biodegradable PLA has attracted increasing attention as a candidate for us in industrial applications since it possesses excellent mechanical properties (especially in tensile strength and modulus) and is produced with corn or other starches as the starting raw material.⁷⁻⁹ With these advantages, PLA is a versatile material with applications in the medical, textile, and

packaging fields. However, PLA is rigid and brittle at room temperature due to its glass transition temperature (T_g) close to 55 °C, which limiting its melt processability and its end-use mechanical performance. An improvement of the toughness of such brittle polymers can generally be achieved by blending a ductile secondary phase into the base polymer. PCL, a ductile biodegradable polymer, has been chosen as a blending partner for PLA,¹⁰⁻¹⁵ and the fracture properties of PLA/PCL are found to be greater than those of pure PLA. However, it is also found that the immiscibility of PLA and PCL causes phase separation, and tends to lower the fracture properties.¹⁰ Some references verify that such immiscibility can be improved by adding lysine triisocyanate (LTI) as a compatibilizer. As a result, the fracture toughness of PLA/PCL can enhance effectively due to the addition of LTI.^{16,17}

Presently, there have been quite a few investigations dealing with the phase morphology structure, mechanical properties and biodegradability of PLA/PCL blends using as plastic plate and membrane. However, few researchers have focused on the study of structure and property of PLA/PCL blends for melt-blown (MB) nonwoven. Melt-blowing was a one-step process

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to make microfiber nonwovens directly from thermoplastic polymers with the aid of high-velocity air to attenuate the melt filaments. It has become one of the most important industrial techniques in nonwovens because of its ability to produce fabrics of microfiber structure suitable for air and water filtration media. It is estimated that over 90% of all MB nonwovens were made from polypropylene (PP). However, PP is well known as one of the non-biodegradable polymeric materials produced from petroleum resource, which most of its uses related to short life time and white pollution. The literature regarding PLA-based MB is rather limited. Müller and Krobjilowski¹⁸ firstly studied the PLA MB process in 2001 and found that PLA was processable over a wide range of temperatures. Liu and Cheng reported¹⁹ the influence of production processing on the structure, morphology, and mechanical properties of PLA MB nonwoven. In our previous research,^{20,21} the structure and properties of PLA chips and PLA-based composites for melt-blowing nonwovens were analyzed. The research showed the PLA MB has high strength, but low flexibility, which limits its industrial or medicinal application.

The aim of this paper is to present original results obtained in some general work devoted to the design of degradable and flexible PLA-based melt-blown nonwoven materials for filtration applications. Firstly, PLA was mixed with PCL according to different proportion. The 3 wt% tributyl citrate (TBC) of PCL was added in order to improve the miscibility between PLA and PCL. PLA/PCL blends were obtained by use of the twin-screw extruder. Subsequently, the influence of the introduction of PCL on the microstructures and crystallization of blends was carefully investigated by means of field emission scanning electron microscope (SEM). The thermal properties of pure PLA and PLA/PCL blends were analyzed by differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA). The crystalline structure of pure PLA and blends was analyzed by X-ray diffractometer (XRD). Finally, their rheological behavior was studied using a Rosand RH7 Walvern Capillary Rheometer.

Experimental

Materials. PLA, 6252D, with specific gravity 1.24 g/cm³ and melt flow index (MFI) 80.0 g/10 min (210 °C, 2.16 kg) was supplied by nature works (Minnetonka, MN, USA). PCL was purchased from Shenzhen Esun Industrial Co., Ltd (Guangdong, China). Its number average molecular weight is 80000 g/mol. Tributyl citrate (TBC), with the density of 1.039-

1.044 g/cm³ and the number average molecular weight of 360.45 g/mol, was brought from Tianjin Chemical Reagent Research Institute (Tianjin, China).

Preparation of PLA/PCL Blends. PLA pellets were dried in a vacuum oven at 98 °C for 3 h. PCL pellets were carefully desiccated for 12 h in a vacuum oven at 50 °C. PLA/PCL blends with various components was prepared by physical melting blending method. The 3 wt% tributyl citrate (TBC) of PCL was added as compatibilizer. The preparation processes of PLA/PCL blends were performed in two steps. In the first step, PLA chips were compounded with PCL chips and TBC by the high speed mixer (SHR-10A, Zhangjiagang City Yili Machinery Co., Ltd, China). Next, PLA/PCL blends with various components were prepared and pelletized by a conventional twin-screw extruder (TSE-30A, Nanjing Ruiya Extrusion System Co., Ltd, China). The resulting composites were dried for 12 h in a vacuum oven at 50 °C for measurement. Blends with the 1, 3, and 5 wt% PCL content were marked by PLA/PCL-1, PLA/PCL-3, and PLA/PCL-5, respectively, in this paper.

Blends Properties. SEM: The surface microstructure of pure PLA and PLA/PCL blends with various components was investigated by SEM. The SEM observations were conducted with JSM-5610LV SEM machine. The samples were previously sputter-coated with a gold layer to avoid charging. The acceleration voltage used was 5 kV.

DSC: DSC was performed on Perkin Elmer Diamond DSC in order to study the thermal properties of pure PLA, PCL and PLA/PCL blends. The samples were heated from 20 to 200 °C at 10 °C/min under nitrogen atmosphere and kept at 200 °C for 3 min to eliminate the previous thermal history, and then quenched to the ambient temperature. The samples were heated again to 200 °C at 10 °C/min to evaluate the melting behavior. The thermal properties, such as glass transition temperature (T_g), cold crystallization temperature (T_c) and melt temperature (T_m) were determined from the heating scan of the samples. The relative degree of crystallization (X_c) of PLA, PCL and blends was estimated from the corrected enthalpy, using the ratio between the heat of fusion of the studied polymer and their heat of fusion of the totally crystalline polymer, *i.e.*

$$X_c = \frac{\Delta H_c}{\Delta H_m^0} \quad (1)$$

Where, ΔH_c is the enthalpy of fusion of the studied samples and ΔH_m^0 is the enthalpy of fusion of a totally crystalline material. The used in eq. (1) was 93 J/g for PLA²² and 136 J/g for

PCL.²³

TGA: TGA of pure PLA and PLA/PCL blends was performed on a Perkin Elmer Pyris to study their thermal stability. The scanning rate was at 10 °C/min and the temperature range was from 23 to 600 °C in N₂ atmosphere.

XRD: The microstructure and crystallization of pure PLA and PLA/PCL blends were analyzed by Rigaku D/MAX XRD using CuK_α radiation with a wave length (λ) of 1.542 nm. The angle of incidence was varied from 4° to 50° by steps of 0.02 s. The accelerating voltage was 40 kV, and the tube current was 150 mA. All measurements were performed at room temperature.

Rheological Behavior: The rheological behavior of pure PLA and PLA/PCL blends were studied using a Rosand RH7 Walvern Capillary Rheometer at 220 °C. The diameter of the capillary was 1.00 mm and the L/D ratio of the capillary was about 32.

Result and Discussion

SEM. SEM micrographs of the pure PLA and PLA/PCL blends with various components surfaces were shown in Figure 1. Obviously, the surface of pure PLA is homogeneous phase structure (Figure 1(a)). As little PCL is introduced

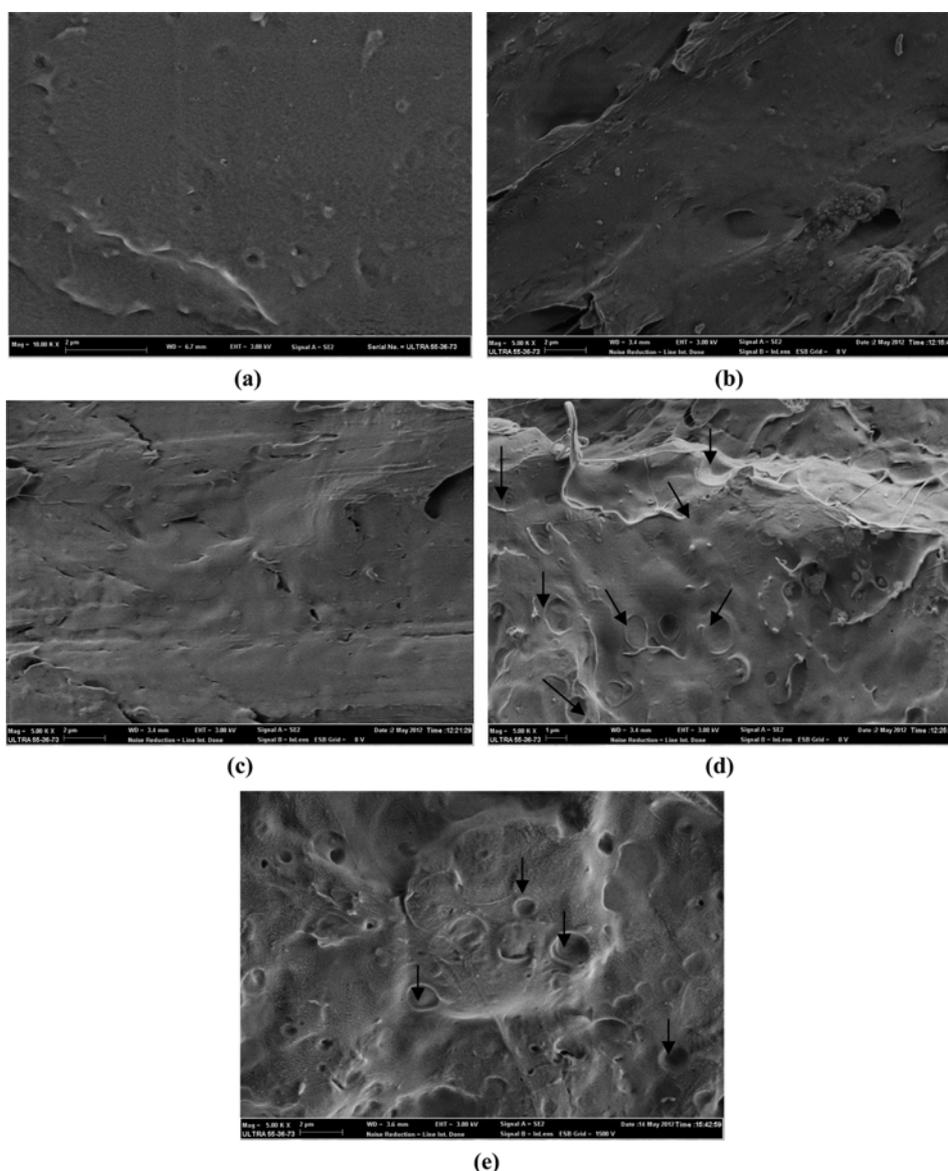


Figure 1. SEM micrographs of the pure PLA and PLA/PCL blends with various components: (a) pure PLA; (b) PLA/PCL-1; (c) PLA/PCL-3; (d) PLA/PCL-5; (e) PLA/PCL-5 without TBC.

(showed in Figure 1(b) and Figure 1(c)), the cross-section of PLA/PCL blends still keep the same phase structure with the same as the pure PLA. As shown in Figure 1(d), some small circular parts are observed in PLA matrix with 5 wt% PCL. The circular structures (marked by arrows) with indistinct interfaces observed in PLA/PCL blends are the spherulites of PCL, according to the Todo *et al.*²⁴ reports. SEM of PLA/PCL blends without TBC shows that sea-island structure and phase interfaces become distinct (marked by arrows) compared with that of PLA/PCL blends with TBC, as shown in the Figure 1(e). The well miscibility of PCL and PLA can be attributed to good interaction PCL with PLA when TBC is added as compatibilizer. Xiao and Yang²⁵ and Wang *et al.*¹² research showed the same results. The reason is that TBC cause transesterification reaction between PLA and PCL which decreased the dispersed phase size and improve the compatibility.

DSC. DSC curves of pure PLA, PCL and PLA/PCL blends with various components were plotted in Figure 2. Some thermal characteristic parameters from Figure 2 were listed in Table 1. It can be seen that there are two peaks in DSC curves

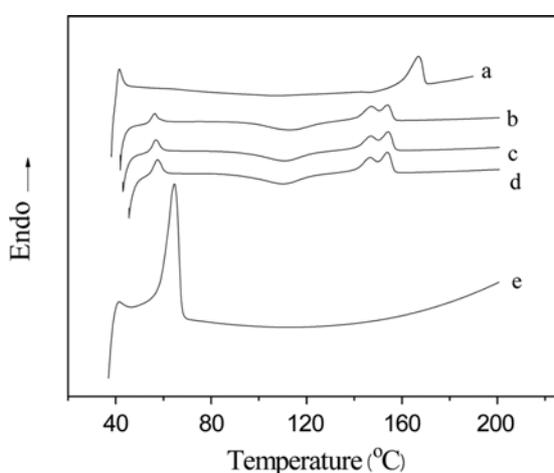


Figure 2. DSC curves of pure PLA, PCL and PLA/PCL blends with various components: (a) pure PLA; (b) PLA/PCL-1; (c) PLA/PCL-3; (d) PLA/PCL-5; (e) pure PCL.

of pure PLA (Figure 2(a)). The peak at low temperature corresponds to the glass transition temperature (T_g) of pure PLA, and the peak at high temperature reflects its melting process. It is known that the T_g and melting temperature (T_m) of pure PLA are 41.7 and 167.1 °C, respectively. The heating curve of PCL just appears a melting peaking at about 64.8 °C (Figure 2(e)) because of its low T_g beyond our measurement temperature.⁵ As shown in Table 1, the T_g values of PLA/PCL blends are higher than that of pure PLA and have no change as the increasing of PCL content. This phenomenon suggested the presence of the interactions caused by TBC between PCL and PLA. The interactions restricted the mobility and diffusion of the PLA chains during the glass transition. The low heat distortion temperature of PLA was a disadvantage in the normal application of PLA-based melt-blown nonwoven materials. The increased T_g suggested that the PLA/PCL composites can tolerate higher application temperature than the pure PLA can.

An exothermic peak corresponding to the cooling crystallization process of PLA can be seen at about 110 °C for in DSC curves of PLA/PCL blends. These cooling crystallization peak point values (T_c) decrease with the increase of PCL content. PLA is semicrystalline polymer and its mechanical and physical properties are governed by the crystal microstructure. For PLA/PCL blends, the introduction of PCL and compatibilization of TBC affect the interactions among the PLA chains. The changed interfacial interactions further affects the crystallization behavior and the physical structure of PLA. This can be attributed to the nucleating effect of PCL in PLA cooling crystallization process.

Additionally, there are two melting peaks at high temperature of DSC curves of blends. The two melting peaks correspond to the melting of small and unperfected crystal and PLA, respectively. Both of lower melting peaking value (T_{m1}) and higher melting peaking value (T_{m2}) of blends are lower than that of pure PLA. As we all known, the blends can crystallize more quickly than neat PLA as PCL works as a nucleating agent of PLA. However, the formed crystalline structure

Table 1. Thermal Characteristic Parameters of Pure PLA, PCL, and PLA/PCL Blends with Various Compositions

Sample	T_g	T_c	T_{m1}	T_{m2}	X_c	T_{d10}	T_{d80}	T_d	X_{cx}
Pure PLA	41.7	-	-	167.1	0.261	380.6	421.7	430	0.385
PLA/PCL-1	56.8	112.2	147.4	154.2	0.259	347.7	400.1	412.6	0.336
PLA/PCL-3	57.2	110.9	146.8	154.6	0.231	361.9	406.1	420.7	0.286
PLA/PCL-5	57.6	108.9	146.5	153.8	0.222	362.5	411.2	424.5	0.261
PCL	-	-	64.8	-	0.520	-	-	-	0.530

by the heterogeneous nucleation was less complete than that of PLA, for example, with thinner and/or less perfect crystalline lamella. Thus, small melting peak belong to the melting of less perfect crystal appears before PLA melting peak. The result is also able to be proved by the relative degree of crystallization (X_c) values of blends, calculated by eq. (1). The data from Table 1 show that PLA/PCL blends have lower X_c values than that of pure PLA. On the other hand, these less perfect structure led by the presence of PCL also decreased the melting temperature of blends.

TGA. The thermal stability and degradation profiles of pure PLA and PLA/PCL blends with various components based on TGA were plotted in Figure 3. All of thermogram tracing of PLA and PLA/PCL blends exhibits a single weight loss step with the beginning decomposition temperature at about 297 °C. And the thermal decomposition process of PLA/PCL blends is found to be stable in the temperature range of about 23-297 °C. The decomposition temperature at 10% weight loss (T_{d10}), at 80% weight loss (T_{d80}) and the final decomposition temperature (T_d) of pure PLA and blends were listed in Table 1, respectively. In weight loss terms, the T_{d10} , T_{d80} , and T_d of pure PLA are 380.6, 422.7, and 430 °C, respectively. The T_{d10} , T_{d80} , and T_d values of blends reduce as PCL is added, whereas slightly increase with the increase of PCL content, which can be attributed to the presence of TBC. The improved miscibility between PLA and PCL by TBC caused the good interface effect, which favors for heat transfer, diffusion and the melt of the PCL with low T_m , resulting in deterioration of the thermal stability of blends.

XRD. XRD patterns of pure PLA, PCL and PLA/PCL

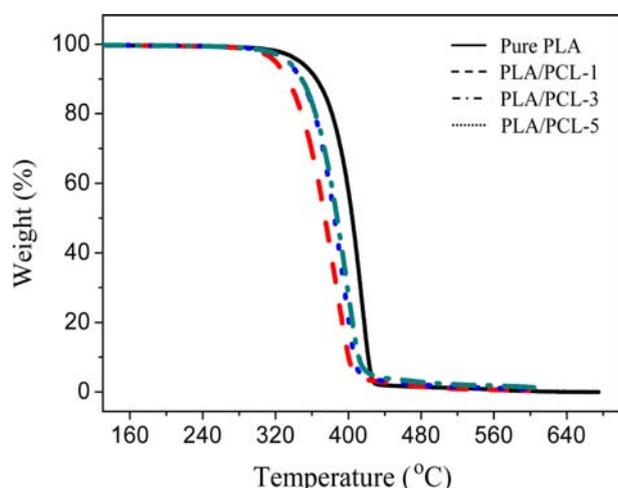


Figure 3. TGA thermograms of pure PLA and PLA/PCL blends.

blends were shown in Figure 4. The diffraction pattern of pure PLA shows essentially two sharp diffraction band characteristic of the crystalline phase (Figure 4(a)) and these sharp crystalline peaks at $2\theta = 16.53^\circ$ and 18.88° . According to the literature,²⁶ these diffractions can be assigned to the α -form crystal of PLA. Whereas, PCL pattern is characterized by two peaks approximately at $2\theta = 21^\circ$ and 23.5° corresponding to the (110) and (200) planes respectively.²⁷ For PLA/PCL-1, the location of crystalline peak has no change, compared with pure PLA. As the content of PCL reaches 3 and 5 wt%, a weak crystalline peak appears at $2\theta = 21.64^\circ$, attributing to the crystalline peak of PCL. The diffraction peaks of all of blends present lower intensity than those of pure PLA. XRD of the polymer matrix is influenced by the presence of the fillers, either in the case of PLA or in that of PCL. The relative degree of crystallization (X_{cx}) of pure PLA and blends is calculated from Figure 4 by means of the following relationship;

$$X_{cx} = \frac{I_c}{I_c + I_a} \quad (2)$$

Where I_c and I_a are respectively the integrated intensities of the crystalline and amorphous phases. X_{cx} values of neat PLA, PCL and blends were listed in Table 1. The X_{cx} values of pure PLA and PCL are 0.385 and 0.530, respectively. For PCL (Figure 4(e)), the crystalline peaks (at $2\theta = 21.64$ and 23.92) are much more intense than for PLA. Such high crystallinity of PCL was previously reported by several authors.²⁸⁻³⁰ The X_{cx} values of PLA/PCL blends are always smaller than that of pure PLA and decreased with increase of PCL content, which con-

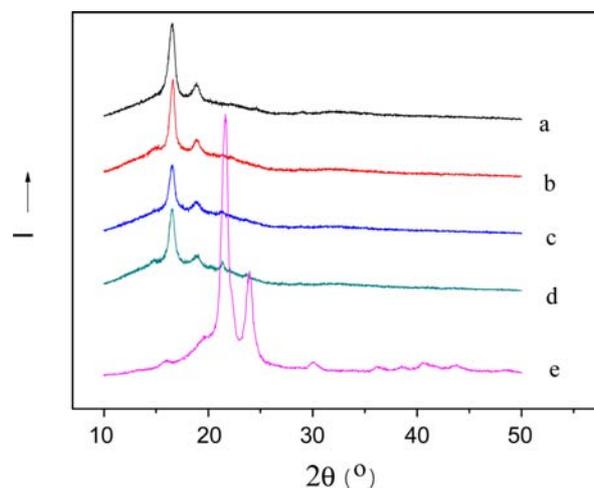


Figure 4. XRD patterns of pure PLA, PCL and PLA/PCL blends: (a) pure PLA; (b) PLA/PCL-1; (c) PLA/PCL-3; (d) PLA/PCL-5; (e) pure PCL.

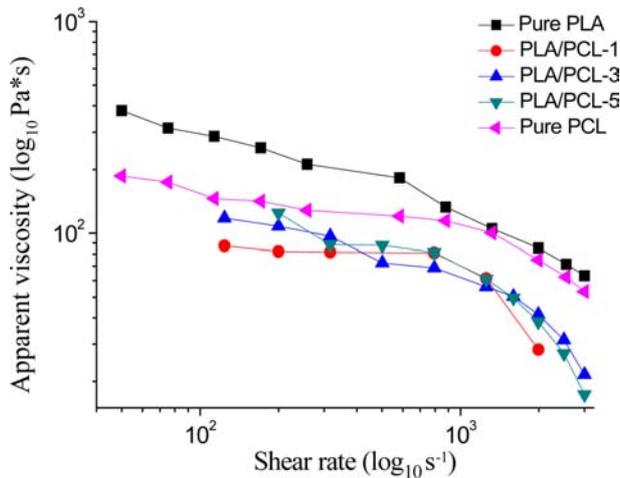


Figure 5. Rheological behaviors of pure PLA, pure PCL and PLA/PCL blends.

sists with the results of DSC. These results quantitatively validate that the crystallization of PLA is attenuated by mixing with PCL.

Rheological Behavior. Figure 5 shows the rheological behavior of pure PLA, pure PCL and PLA/PCL blends. In Figure 5, the apparent viscosity of all samples decreases as the shear rate increases. That is an indication of a pseudo plastic behavior of the melts at 220 °C. Apparent viscosity of blends is smaller compared with pure PLA and pure PCL. There are two reasons for the decrease of apparent viscosity of blends. Firstly, the addition of a small quantity of PCL expands the distance of PLA molecule chain and therefore decreases its apparent viscosity.³¹ In addition, transesterification reaction between PLA and PCL may happen. Transesterification reactions of polyesters are often associated with of the decrease in molecular weight and the broadening of molecular weight distribution which results in the decrease the apparent viscosity of PLA/PCL blends compared that of pure PLA and pure PCL.¹²

Conclusions

PLA/PCL blends with various components for melt-blown nonwoven were prepared by the twin-screw extruder. The 3 wt% TBC of PCL was added as compatibilizer on account of the poor miscibility between PLA and PCL. Microstructure PLA/PCL blends was investigated by SEM. Small circular particle of PCL was dispersed in PLA matrix uniformly. The well dispersion of PCL in PLA matrix could be attributed to good interaction PCL with PLA due to the compatibilization of TBC. Thermal properties of pure PLA and blends were studied

by DSC and TGA. The results from DSC revealed that PLA/PCL blends had higher T_g , lower T_m and X_c value. The cooling crystalline peak of blends appeared and the T_c values decreased with the addition of PCL and increasing of PCL content, indicating the heterogeneous nucleation effect of PCL on the crystallization PLA. The thermal stability of blends decreased due to the introduction of PCL, while their degradation temperature could be increased with the increasing of PCL content. Crystalline structure of pure PLA, PCL and blends was analyzed by XRD. The results showed that pure PLA was semi-crystalline in the formation α -crystal and PCL had stronger diffraction peak and the higher relative degree of crystallization. The diffraction peak of PCL reflected at around $2\theta=21.64^\circ$ of diffraction patterns of blends. The weaker crystalline diffraction peak and lower X_{cx} values of blends validated that the crystallization of PLA was attenuated by blending with PCL. Finally, the rheological behavior of pure PLA and PLA/PCL blends were tested. All of samples had the flow properties of shear thinning in molten state.

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