

## PLA/PCL 필름의 인장 및 장벽 특성에 미치는 PCL과 상용화제의 영향

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## Effect of PCL and Compatibilizer on the Tensile and Barrier Properties of PLA/PCL Films

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**Abstract:** In this work, the blend films of poly(lactic acid) (PLA) and poly( $\epsilon$ -caprolactone) (PCL) were prepared by the solvent casting method. The influence of PCL content and compatibilizer on the structure, tensile and barrier properties was studied. The results indicated that PCL showed good dispersion in PLA matrix as tributyl citrate (TBC) was added as a compatibilizer. PCL showed a promotion effect on the crystallinity of PLA/PCL films. The compatibility of PLA and PCL was improved by TBC. The tensile modulus and the elongation at break of PLA/PCL films increased to various extents due to the input of PCL and TBC compared to pure PLA film. The improvement of oxygen and water vapor barrier properties of the blend films were provided and depended on the content of PCL and the appearance of TBC. The transparency of the blend films decreased with the increase of the PCL content.

**Keywords:** poly(lactic acid), poly( $\epsilon$ -caprolactone), structure, mechanical properties, barrier properties.

## Introduction

Due to a number of environmental problems caused by the traditional oil derived polymers, poly(lactic acid) (PLA), a bio-based and biodegradable polymer, is currently receiving a great deal of attention for various applications such as packaging films, biomedical materials, and textiles.<sup>1-4</sup> PLA is a type of biodegradable aliphatic polyesters from renewable resources, with the monomer produced by fermentation of polysaccharides. It has moderate modulus and good processability, comparable to many petroleum-based plastics. Therefore, PLA is now being produced on a commercial scale by a number of

companies. However, high brittleness, low thermal resistance and limited gas barrier properties hinder its wide spread application.<sup>5</sup> One of the classical ways to overcome these problems is to perform blending with another polymer. Blending allows obtaining new materials with improved properties and is less costly than chemical modifications or synthesis of new, tailor-made macromolecules.

According to recent studies, blends of the biodegradable, ductile poly( $\epsilon$ -caprolactone) (PCL) with PLA are an alternative way of achieving novel biodegradable materials with desired properties.<sup>6,7</sup> The addition of PCL not only is a good strategy for improving the mechanical properties of PLA, but it retains its biodegradability.<sup>8,9</sup> However, it is known that, like most polymer blend couples, PLA and PCL are thermodynamically immiscible.<sup>6,7,10-15</sup> Therefore, good dispersion and compatibility of this immiscible polymer couples are of prime

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importance for the preparation of PLA/PCL blends. Considerable efforts have been made to enhance the miscibility between PLA and PCL by using generally known techniques. Maglio *et al.*<sup>13</sup> and Dell'Erba *et al.*<sup>14</sup> prepared triblock poly(*L*-lactic acid) (PLA)-PCL-PLA copolyesters that acted as compatibilizer of PLA/PCL blend, resulting in an increase of the elongation at break of the blends from 2 to 53% and a smaller size of the dispersed phase. The di-block PLA-PCL copolyester has also been used as a compatibilizer between PLA and PCL.<sup>15,16</sup> They showed that the elongation at break of the PLA/PCL blends with the di-block PLLA-PCL increased to 71.4% compared to the 2% of those blends without this compatibilizer. In addition, some PLA/PCL blends have been prepared by the addition of small molecule compatibilizers, such as glycidyl methacrylate (GMA), dicumyl peroxide (DCP) and lysine triisocyanate (LTI).<sup>17-22</sup> The results showed that the incorporation of these small molecule compatibilizers could, to some extent, reduce the size of the dispersed phase and improve the toughness of the PLA matrix. However, these compatibilizers are difficult to prepare or have high toxicity and thus are unsuitable for being added into environmentally-friendly material.

Additionally, environmental concerns and disruptions of oil resources have led to increasing requirements for the use of biodegradable PLA as packaging materials. The main limitations of PLA as a packaging material are its high gas permeability (O<sub>2</sub>, water vapor, CO<sub>2</sub>, etc.) and a low ductility.<sup>23-26</sup> Only a few researchers have studied the influence of the addition of inorganic particles on the barrier properties of PLA/PCL blends. Cabedo *et al.*,<sup>27</sup> for instance, blended PLA/PCL with nanoclay and evaluated the effect of blending and nanoclay addition on the mechanical, thermal and gas barrier properties of this mixed system. Jain *et al.*<sup>28</sup> investigated the influence of talc loading on the phase morphology and the tensile and barrier properties of PLA/PCL/talc composites. However, in our paper, we particularly considered PLA as a highly promising packaging film and paid attention to the effect of PCL loading on the barrier properties of the PLA/PCL blends for the films.

Therefore, the objective of this work was to obtain PLA/PCL films with the desired barrier properties by a solvent casting method; although not applicable for commercial production, the results show the effects of optimum mixing. Because of the immiscibility of the two components, the safe and cheap tributyl citrate (TBC) was adopted as the compatibilizer. The effect of the PCL contents and TBC on the phase morphology,

crystalline structure, miscibility, and the mechanical and gas barrier properties of blended films with various compositions were investigated. The results permitted discussions of some of the relationships among structure and the mechanical and barrier properties of the films.

## Experimental

**Materials.** A commercial PLA (3051D, NatureWorks, USA), with specific gravity 1.25 g/cm<sup>3</sup>, molar mass of ca.  $1.42 \times 10^4$  g/mol, and melt flow index (MFI) 7.75 g/10 min (210 °C, 2.16 kg) was used; it was semicrystalline. PCL was purchased from Shenzhen Esun Industrial Co., Ltd. (China). Its number average molecular weight was 80000 g/mol. Tributyl citrate (TBC), with a density of 1.039-1.044 g/cm<sup>3</sup> and molecular weight of 360.45 g/mol, was bought from Tianjing Chemical Reagent Research Institute (China). Dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>), with a density of 1.320-1.330 g/cm<sup>3</sup>, was provided by Gaojing Fine Chemistry Co., Ltd. (China).

**Preparation of PLA/PCL Films.** Prior to the mixing step, the PLA pellets were dried in a vacuum oven at 95 °C for 8 h. PCL pellets were carefully desiccated for 12 h, being turned over once every two hours, in a vacuum oven at 50 °C. PLA/PCL films with various compositions were prepared by a solvent casting method. The blending ratio of PLA/PCL blends was 99/1, 97/3 and 95/5 wt%, and these blends were dissolved in CH<sub>2</sub>Cl<sub>2</sub> in proportion of 1/10 (wt/wt) (i.e. PLA/PCL blends :CH<sub>2</sub>Cl<sub>2</sub>=1:10). The solutions were vigorously stirred for 3 h at room temperature (RT) before they were poured into a 9 cm diameter polytetrafluoroethylene Petri dish. Then the solution was allowed to dry for about 24 h in a fume cupboard at RT. The resultant films, with a thickness of ca. 0.1 mm, were peeled from the Petri dish after drying. The obtained films were labeled, respectively, as PCL1, PCL3 and PCL5 in this paper. Additionally, modified PLA/PCL films with the same PCL proportions were prepared by the addition of 3% tributyl citrate (TBC) of the PCL weight as compatibilizer under the same processing conditions; these films were labeled PCL1T, PCL3T and PCL5T, respectively. The same mixing procedure was used for pure PLA and pure PCL to compare the pure materials with the blend films.

**Characterization.** The phase morphology of the films was investigated using a scanning electron microscope (SEM, JSM-5610LV, JEOL Co., Japan). The cryogenic cross sections of the PLA/PCL films were prepared in a liquid nitrogen environment and directly pasted, by use of conductive tapes, on

copper sample stages. Then the surfaces of the cross sections of the films were plated with a thin layer of gold before inspection. The acceleration voltage used was 5 kV.

Wide angle X-ray diffraction (WAXD, Rigaku D/MAX, Japan) scans were recorded in reflection using  $\text{CuK}\alpha$  radiation with a wave length ( $\lambda$ ) of 0.1542 nm at RT. The angle of incidence was varied from 8° to 50° in steps of 3°/min. The accelerating voltage was 40 kV, and the tube current was 150 mA.

Dynamic-mechanical thermal analysis (DMA) was performed with a DMA Q800 (TA Instrument Co., USA). The following parameters were fixed for the DMA measurements: constant frequency of 1 Hz and temperature range of 25–120 °C for the pure PLA film, -100, -50 °C for the pure PCL film and -100, -120 °C for PLA/PCL films, heating rate of 3 °C/min and gap distance of 20 mm. The strain amplitude was selected after preliminary strain sweep tests in order to maintain the linear viscoelasticity regime during the measurements. The samples were prepared by cutting strips from the films with a width of 6 mm.  $\tan \delta$ , the glass transition temperatures ( $T_g$ , as the  $\tan \delta$  peak temperature), and storage modulus ( $G'$ ) were evaluated.

Mechanical behaviors of neat PLA films and PLA/PCL films were evaluated by tensile tests on the basis of GB/T13022-1991. Film samples were cut into rectangular shapes of 150 mm width and 900 mm length. Mechanical properties of the neat PLA and the PLA/PCL films were measured with a universal strength tester (Labthink Instruments Co., Ltd., China). Samples were conditioned for 48 h at 23 °C and 50% RH in a constant temperature and humidity chamber before the measurements. The initial grip separation and the crosshead speed were set at 50 mm and 50 mm/min, respectively. Tensile strength, tensile modulus and the elongation at break were calculated by at last five replicates.

Oxygen permeability coefficients (OP ( $\text{cm}^3 \cdot \text{cm}/(\text{cm}^2 \cdot \text{s} \cdot \text{Pa})$ ) of the neat PLA and PLA/PCL films were characterized with a VAC-V1 gas permeability tester (Labthink Instruments Co., Ltd, China) on the basis of GB/T1038-2000. The tests were carried out at 23±2 °C, and 50% relative humidity. The measuring area of the circular films was about 38.46  $\text{cm}^2$ . Two replicates were conducted for each sample. Firstly, the oxygen transmission rate (OTR ( $\text{cm}^3/(\text{m}^2 \cdot \text{day} \cdot \text{atm})$ ) values of our films were calculated by eq. (1).

$$\text{OTR} = \bar{P} \times \frac{V}{S} \times \frac{T_0}{p_0 T} \times \frac{24}{\Delta p} \quad (1)$$

where  $\bar{P}$  is the arithmetical mean value of the change of gas pressure per unit time in the testing chamber,  $V$  is the volume

of the testing chamber,  $T$  is the temperature as the samples are being tested,  $\Delta P$  is the actual difference in partial gas pressure between the two sides of the samples; the temperature under standard condition ( $T_0$ ) and the pressure under standard condition ( $p_0$ ) value were 273.15 K and 1.0133  $\times 10^5$  Pa, respectively. Then, the OP values of the films were calculated by eq. (2)

$$\text{OP} = 1.1574 \times 10^{-9} \times \text{OTR} \times d \quad (2)$$

where  $d$  is the thickness of samples.

Water vapor permeability coefficients (WVP ( $\text{g} \cdot \text{cm}/(\text{cm}^2 \cdot \text{s} \cdot \text{Pa})$ ) values of the neat PLA and PLA/PCL films were measured gravimetrically using a TSY-T3 WVP tester (Labthink Instruments Co., Ltd., China) according to GB/T16928-1997. Tests were performed at 38±0.2 °C and 90% RH. Two samples with about 33  $\text{cm}^2$  areas were tested for each film type. The WVP value was calculated using eq. (3).

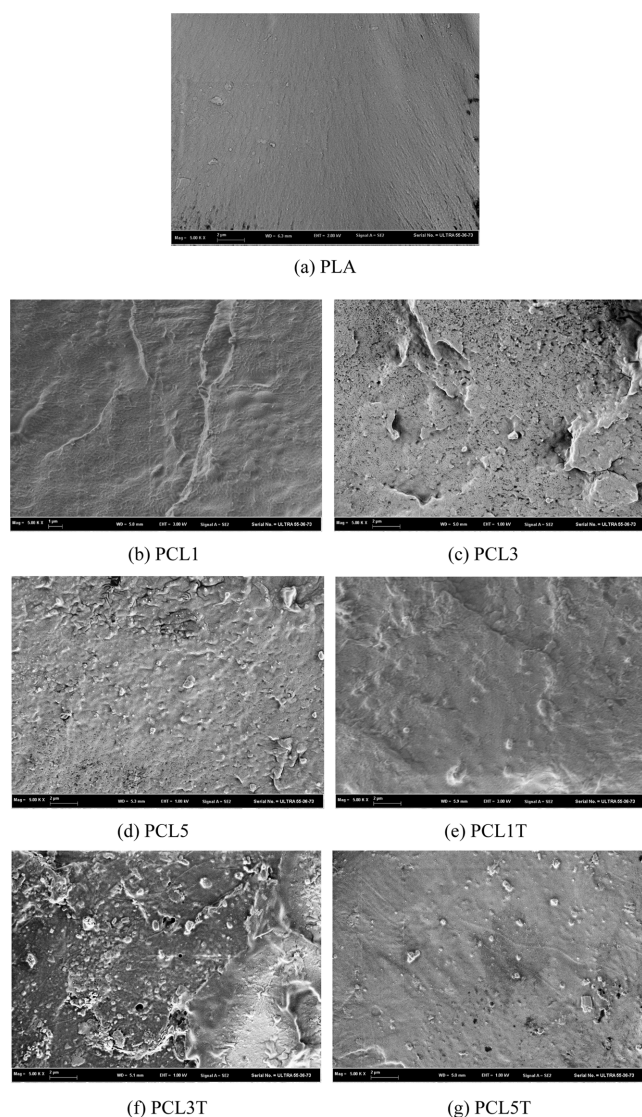
$$\text{WVP} = 1.157 \times \text{WVT} \cdot d / \Delta p \quad (3)$$

where WVT is the water vapor transmission rate through a mean film thickness  $d$ ,  $\text{WVT} = \frac{\Delta m \times 24}{A \cdot t}$ , ( $\Delta m$  is the incremental quality of films at specific intervals of time  $t$ ,  $A$  is the area of the tested films), and  $\Delta P$  is the actual difference in partial water vapor pressure between the two sides of the samples.

The transparency of the neat PLA and blend films was determined using a WGT-S light transmittance and haze tester (INESA Instruments Co., Ltd., China).

## Result and Discussion

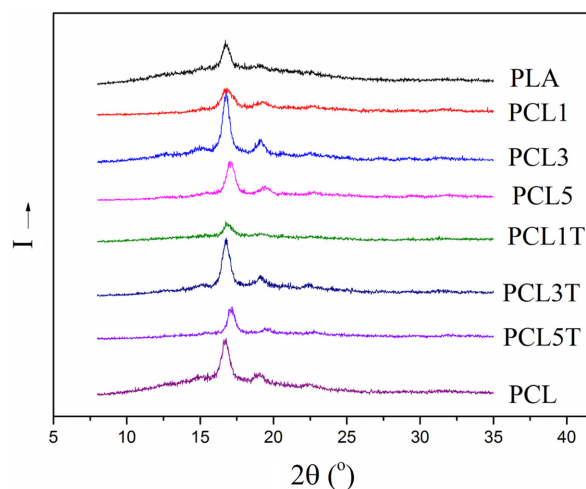
**SEM.** SEM micrographs of cryo-fractured surfaces of the PLA/PCL films with various compositions are shown in Figure 1. Figure 1(a) shows the cryo-fractured surfaces of the PLA film. The pure film exhibits a single phase and uniform structure. In Figures 1(b)-(d), the surfaces of the PLA/PCL films without TBC were rough and uneven. An obvious dispersed phase-continuous phase structure in the films surface could not be observed, although there were a few, possibly PCL, particles on the surface of the PCL3 sample and more protruding from the surface of the PCL5 sample. This phenomenon may be attributed to the addition of only a small amount of PCL and the poor miscibility of PLA and PCL, which has been proven in previous works.<sup>11,12</sup> On the other hand, in Figures 1(e)-(g), the blend films with TBC exhibited



**Figure 1.** SEM micrographs of cryo-fracture sections of pure PLA and PLA/PCL blend films with various compositions: (a) PLA; (b) PCL1; (c) PCL3; (d) PCL5; (e) PCL1T; (f) PCL3T; (g) PCL5T.

a different morphological structure. All of the fracture surfaces were relatively smooth, and the PCL particles on the surface of the PLA/PCL blends with TBC were somewhat more spherical with a less obvious interface for PCL contents of 3 and 5 wt%. It revealed that the presence of TBC, as a compatibilizer, decreased the interfacial tension and improved the dispersion of the PCL phase.

**XRD.** In order to study the effect of PCL content and the addition of TBC on the crystallinity of the PLA matrix, the crystalline structures of pure PLA, pure PCL and PLA/PCL films were characterized by WAXD, as shown in Figure 2. The diffraction profile obtained by WAXD for PLA showed essen-



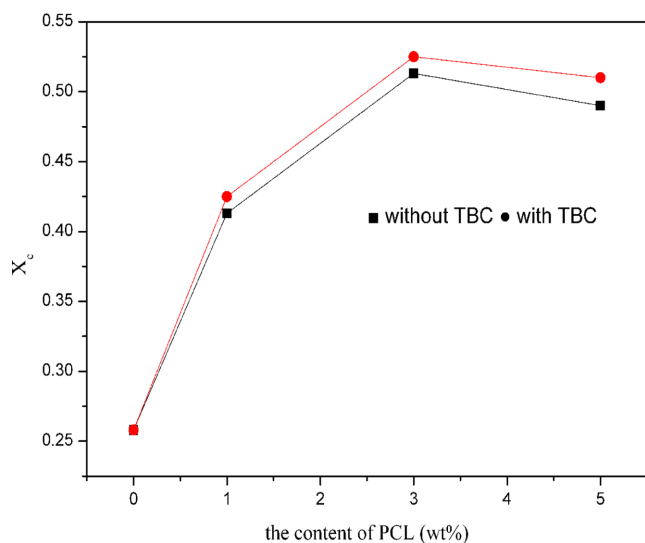
**Figure 2.** WAXD patterns of pure PLA, PCL and PLA/PCL films with various compositions.

tially a large characteristic crystalline peak at  $2\theta=16.8^\circ$ , superimposed on a broad amorphous peak background with a small second peak at  $2\theta=19.1^\circ$ ; this is in agreement with previous papers,<sup>29,30</sup> indicating that the PLA was partially crystalline. The crystalline peaks of PCL were located at  $2\theta=14.8^\circ$ ,  $16.8^\circ$  and  $19.1^\circ$ , with the peaks at  $2\theta=16.8^\circ$  and  $19.1^\circ$  being much more intense than those of PLA. For most of the blend films, their XRD curves retained the characteristic crystalline peak of PLA at  $2\theta=16.8^\circ$ . The intensity of the diffraction peaks at  $2\theta=19.1^\circ$  was slightly enhanced with the incorporation of low content PCL (as shown on diffraction line PCL1 and diffraction line PCL1T). As PCL content reached to 3 and 5 wt%, the intensity of peaks at  $2\theta=16.8^\circ$  and at  $2\theta=19.1^\circ$ , being indicative of the PLA and PCL crystallinities respectively, was increased remarkably. Furthermore, it seemed that the intensity of diffraction peaks of blending films with 3 wt% PCL was the most prominent regardless of whether the TBC was present. It may be that the addition of low content PCL has a heterogeneous nucleation effect on the PLA crystallization, while the effect is weakened as the PCL content increases.

The relative degrees of crystallinity ( $X_c$ ) of pure PLA and the blend films were calculated from Figure 3 by means of the following relationship,

$$X_c = \frac{I_c}{I_c + I_a} \quad (4)$$

where  $I_c$  and  $I_a$  are, respectively, the integrated intensities of the crystalline and amorphous phases. The  $X_{cx}$  values of neat PLA, PCL and blends are listed in Table 1. It was seen that the



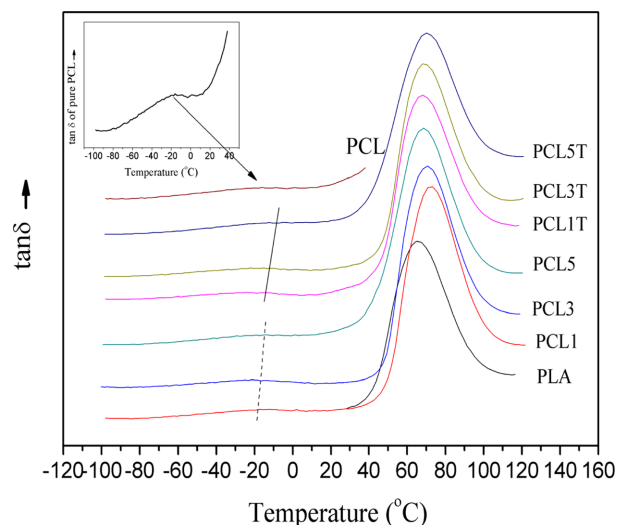
**Figure 3.**  $X_c$  values of PLA and PLA/PCL films with various compositions.

**Table 1. Tensile Properties of PLA and PLA/PCL Films with Various Compositions**

Sample	Tensile strength (MPa)	Tensile modulus (MPa)	Elongation at break (%)
PLA	34.4±1.37	429.3±3.29	2.7±1.67
PCL1	35.5±1.06	433.0±2.91	3.5±1.85
PCL3	36.7±1.23	445.5±2.38	4.7±1.87
PCL5	37.8±1.95	573.8±3.05	6.0±1.36
PCL1T	36.4±2.03	472.0±3.34	5.9±1.91
PCL3T	37.8±1.76	537.3±2.68	7.6±2.13
PCL5T	39.7±1.97	605.1±3.15	8.5±1.97

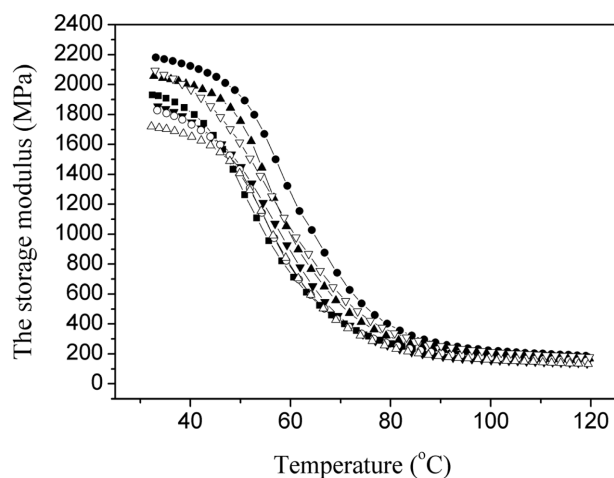
relative degree of crystallinity ( $X_c$ ) of PLA calculated with the software was 35.9%. The  $X_c$  value obtained from the profile of PCL was 55.2%. A high crystallinity of PCL has previously been reported by several authors.<sup>31,32</sup> The  $X_c$  values of the blended PLA film increased with the input of PCL and TBC. It further confirmed that the addition of PCL had a good promotion effect on crystallization of PLA. Additionally,  $X_c$  values of the blending PLA/PCL films with TBC were higher compared to that of PLA/PCL films without TBC, indicating that the improved miscibility of PLA and PCL intensified the promotion effect of PCL on crystallization of PLA.

**DMA.** Figure 4 displays the  $\tan\delta$  spectra of neat PLA, neat PCL and the PLA/PCL films with various compositions. The temperatures at the peaks of the  $\tan\delta$  curves were also considered as the  $T_g$  of the material. Generally, in the field of polymer blends, the location and number of  $T_g$  values can be used



**Figure 4.**  $\tan\delta$  spectra of neat PLA, PCL and PLA/PCL films with various compositions.

as a criterion to judge whether the components of a binary polymer blend are miscible or not. The  $T_g$  of the pure PLA film was about 67.9 °C under our DMA experimental conditions, which was not far from the value of PLA films (67 °C) obtained previously, for instance by Martin and Ave'rous<sup>34</sup> under slightly different conditions. For PCL films, the  $\tan\delta$  peak was much wider and was situated at a lower temperature,  $T_g = -19.4$  °C in our research. In their work Ave'rous *et al.*<sup>35</sup> observed the glass transition at  $T_g = -50$  °C for PCL. The deviation is suggested to be due to the difference of PCL grade and measurement conditions.  $T_g$  values of the PLA/PCL films at higher temperature slightly increased with the addition of PCL from 67.9 to 69.2 °C.  $T_g$  values of the blend films without TBC corresponding to lower temperature was almost unchanged. The result reveals the immiscibility of PLA and PCL. It is essential for compatibilization of immiscible polymer blends that the compatibilizer should locate at the interface between the phases where it is most needed.<sup>36</sup> In comparison with a polymeric compatibilizer, a monomeric compatibilizer can diffuse more easily to the interfaces between the phases of the immiscible polymers.<sup>17</sup> Thus, in our study, TBC was chosen as a monomeric compatibilizer of PLA and PCL. Figure 4 indicates that when TBC was input, the  $T_g$  values of PLA/PCL films at lower temperature exactly increased from -21.3 to -12.4 °C as the PCL content increased from 1 to 5 wt%. From the above results, it is suggested that PLA and PCL are partly miscible in view of the presence of TBC. The result is consistent with the above mentioned SEM conclusion.



**Figure 5.** Storage modulus ( $G'$ ) of pure PLA and PLA/PCL films with various compositions under different temperatures: ■ PLA; ● PCL1; ▲ PCL3; ▼ PCL5; ○ PCL1T; △ PCL3T; ▽ PCL5T.

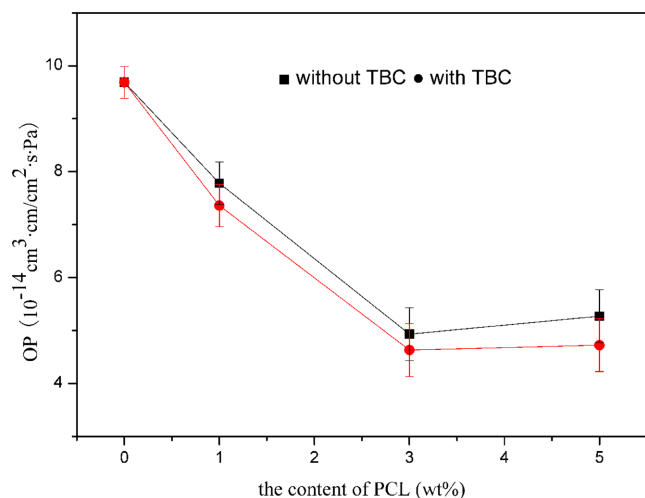
To further study the effect of PCL and TBC on the dynamic-mechanical properties of PLA, the temperature dependence of  $G'$  of PLA and the blend films was determined, as shown in Figure 5. The figure shows that the  $G'$  value of neat PLA at 30 °C (in the glassy state) was around 1930 MPa, but then dramatically decreased with increasing temperature. As the temperature continually increased and approached to 100 °C (at rubbery state), the  $G'$  value of pure PLA gradually tended to constant. Compared to pure PLA films, the  $G'$  values of the PLA/PCL films showed an increment with the incorporation of PCL below and around the glass transition region, from ca. 45 °C to ca. 73 °C. This behavior indicated that the addition of PCL had a considerable effect on the elastic properties of the corresponding PLA matrix. The result is in agreement with those from WAXD, the higher relative degree of crystallinity values caused by the addition of PCL were also involved in the increased rigidity of the molecular chains.

**Mechanical Properties.** The effect of PCL on the tensile properties of the PLA/PCL films with various compositions is summarized in Table 1. The tensile strength and modulus of the pure PLA film were  $34.4 \pm 1.37$  and  $429.3 \pm 3.29$  MPa, respectively. Additionally, the elongation at break of the pure PLA film was  $2.7 \pm 1.67\%$ , showing limited toughness. The tensile strength of the PLA/PCL films increased 3%-10% for the films without TBC and 6%-15% for the films with TBC, with increasing PCL content, respectively. These results suggest a slight contribution of PCL and TBC to the strength of the PLA/PCL films. Similarly, at the low content of PCL, the tensile modulus values of the films were almost unchanged

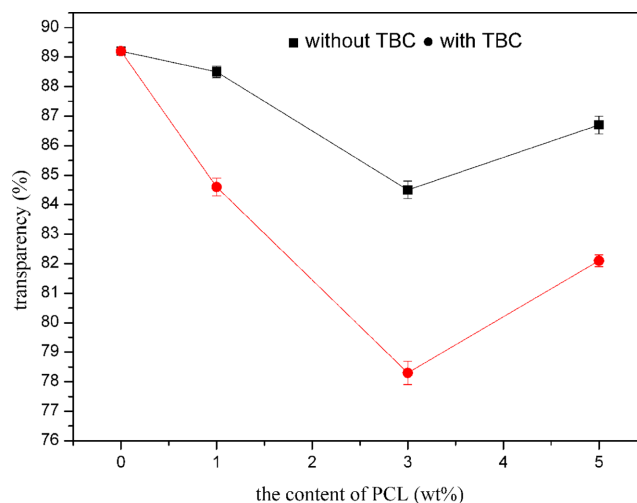
compared to pure PLA film. However, at the higher loadings, the tensile modulus values of the films obviously increased (i.e. 34% for PCL5 and 41% for PCL5T). The enhancement of tensile modulus means higher rigidity of the films, agreeing with the results from DMA. On the other hand, the influence of the addition of PCL on the elongation at break of PLA/PCL films was negligible for the films without TBC. For the films with TBC, their elongation at break had a limited increase when the PCL was added. The elongation at break of a polymer material can be used to evaluate their flexibility. Thus, from the tensile results, the films with PCL and TBC had higher tensile modulus, and slightly higher flexibility but the toughening effect of PCL on PLA was limited.

**Barrier Properties.** The OP and WVP values of pure PLA films and PLA/PCL films are reported as a function of the content of PCL in Figures 6 and 7, respectively. The OP and WVP values of the pure PLA films were  $9.69 \times 10^{-14} \text{ cm}^3 \cdot \text{cm}/\text{cm}^2 \cdot \text{s} \cdot \text{Pa}$  and  $7.97 \times 10^{-9} \text{ g} \cdot \text{cm}/(\text{cm}^2 \cdot \text{s} \cdot \text{Pa})$  respectively. Reductions in OP and WVP values with respect to the pure PLA film occurred as PCL was added. Compared with the PLA/PCL films without TBC, the PLA/PCL films with TBC had slightly lower OP and WVP values. These results emphasized the positive effect of PCL, especially when accompanied by the compatibilization by TBC, on the increase in barrier properties of the PLA/PCL films. This effect was confirmed by the highest reduction in OP values (ca. 49.1%) for the PCL3T films and in WVP values (ca. 38.9%) for PCL5T. Furthermore, according to Figure 6 and 7, it seems that the over 3 wt% content of PCL in the film did not much affect on the OP and WVP because it is suggested that higher PCL contents in the film, somehow, can disturb the activity of compatibilizer. It is well known that the gas transport properties of polymer films are strongly influenced by the tortuosity of the gas molecules flow path. The gas permeation proceeds mainly in the amorphous phase of polymer films. By this account, a semi-crystalline polymer is composed by a nearly impermeable crystalline phase dispersed in a permeable amorphous phase. Therefore, any increase in crystallinity leads to a decrease of the gas permeability due to a diminished contribution of the permeable amorphous phase and to enhanced tortuosity of the diffusion path.<sup>37</sup> In our case, the good adhesion between PCL domains and the PLA matrix and higher levels of crystallinity, as shown in the previous analysis, resulted in a longer path length for the diffusion of water vapor molecules and gas, which led to the decrease in the permeation properties of PLA/PCL films, especially for the PLA/PCL films with TBC.

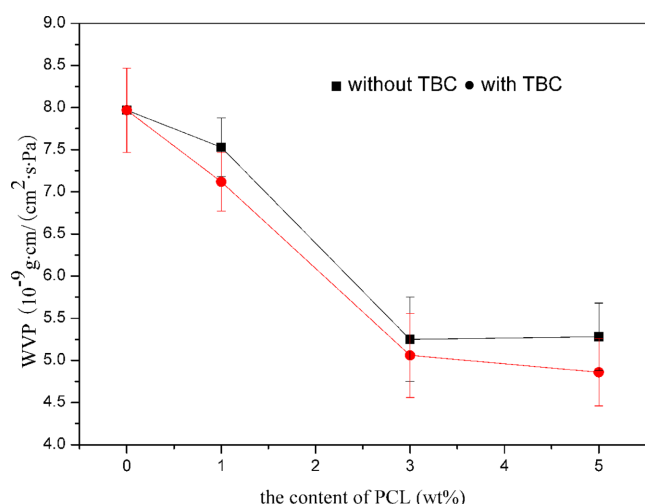




**Figure 6.** OP values of PLA and PLA/PCL films with various compositions.



**Figure 8.** Transparency of PLA and PLA/PCL films with various compositions.



**Figure 7.** WVP values of PLA and PLA/PCL films with various compositions.

As packaging materials, high transparency packaging films can clearly and fully exhibit products, while opaque films sometimes can protect products from the damage of light energy. So, the control of the transparency is an important property for polymer packaging films. In this study, the influence of PCL and TBC on the transparency of the PLA matrix blending films was tested; the results are shown in Figure 8. The transparency of our pure PLA film was about 89%. The transparencies of the blend films were lower than that of the pure PLA films. Moreover, the transparency of blend films with TBC was less than that of the blend films without TBC. In particular, the transparency of PCL3T was the minimum,

78.3%. The reason was considered to be the crystallinity change of the blend films with various compositions. The transparency of polymer films could be related to their crystallinity degree to some extent and the crystalline morphology. Generally, the higher the relative degree of crystallinity, the lower transparency of films.

## Conclusions

PLA/PCL films with various compositions were prepared by solvent casting from  $\text{CH}_2\text{Cl}_2$ . The effects of PCL and TBC on the structure, and the mechanical and barrier properties of the films were investigated. SEM showed that the surfaces of the blend films without TBC were rough and uneven. The PCL could be evenly dispersed in the PLA matrix in the form of spherical structures when TBC was also added. The incorporation of PCL enhanced the intensity of crystalline peak of PLA/PCL films and increased the  $X_c$  values. TBC could improve the miscibility between PLA and PCL which was verified by DMA. The  $G'$  values of pure PLA and the PLA/PCL films decreased with the increase of temperature above the glass transition, as expected. The tensile modulus of PLA/PCL films increased with the increase of PCL and input of TBC. On the other hand, the elongation at break of the PLA/PCL films limitedly increased when TBC was added. For the barrier properties of the blend films, their oxygen and water vapor permeability decreased with the addition of PCL and TBC. Meanwhile, the PLA/PCL films had less transparency than that of the pure PLA film.

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