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## Poly(lactic acid)/Polycaprolactone Blends Compatibilized with Block Copolymer

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### Abstract

This research focused on using a block copolymer of poly(ethylene glycol) and poly(propylene glycol) as a new type of compatibilizer in poly(lactic acid)/polycaprolactone (PLA/PCL) blends. The blends were prepared at 80/20 by a melt blending method, and concentrations of the block copolymer were varied from 0-10 phr. The resultant products were characterized in terms of morphology, mechanical, and thermal properties. It was found that the compatibilized blends exhibited a significant enhancement in tensile strain at break compared to that of the neat PLA/PCL blend, in which the highest strain was obtained at 7.5 phr of block copolymer. Tensile stress of the blends was however declined slightly.

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## 1. Introduction

Recently, biodegradable materials have caught a considerable attention due to increasingly environmental concern, and realization that petroleum resources are finite. Such polymers can be classified into four main groups: natural polymers, such as starch, protein, and cellulose; synthetic polymers from natural monomers, such as poly(lactic acid) (PLA); polymers from microbial fermentation, such as polyhydroxybutyrate (PHB); and petroleum-based polymers such as polycaprolactone (PCL) [1]. PLA is a thermoplastic and derived from biological substrate of maize, cassava, and sugar cane, etc. It possesses high strength and modulus, which is sufficient to apply for automobiles, electric appliances, food packages, and medical devices. To expand its applications, blending with ductile polymers can improve impact resistance and fracture toughness of the base PLA polymer. Blends of PLA with other flexible polymers, such as poly(butylene succinate) (PBS), poly(3-hydroxybutyrate) (PHB), and polycaprolactone (PCL) have been previously studied [2]-[6]. Among these blends, PLA/PCL blends offers an interesting characteristic because of its wide variety of physical property and biodegradability, in which the glassy PLA with high degradation rate shows better tensile strength, while the rubbery PCL with much slower degradation rate shows better toughness. The complementary between these two biocompatible polymers is very important to their blend materials because the performance can be controlled by adjusting the blending ratio and preparation condition to meet various applications [7]-[10]. Rao et al. prepared PLA/PCL (80/20) blends by a melt blending [11]. The blends exhibited the highest elongation and impact strength compared to that of the neat PLA. Rheological study suggested that PCL had higher melt elasticity and viscosity than PLA, and the melt elasticity and viscosity of the blends were increased with the concentration of PCL. Choi et al. compared the effect of two types of compatibilizer in polymer blends (PLLA/PCL): P(LLA-co-CL) and P(LLA-b-CL) on morphology and hydrolysis process [12]. The ratio of PLLA/PCL was controlled at 70/30 by weight and the compatibilizer contents were varied in a range of 5-15%wt. SEM micrograph showed that the combination of P(LLA-co-CL) at 5%wt improved phase compatibility, in which size of the dispersed PCL in the PLA matrix was reduced.

The current research aimed to prepare PLA/PCL blends using a block copolymer of poly(ethylene glycol) and poly(propylene glycol) as a new compatibilizer to improve phase miscibility. The effect of the copolymer on morphology, tensile strength, and thermal property of the blends was examined.

## 2. Experimental

### 2.1. Materials and Blend preparation

Poly(lactic acid) (4042D) was purchased from NatureWorks Co. Ltd. Polycaprolactone (70,000-90,000 g/mol) and block copolymer of poly(ethylene glycol) and poly(propylene glycol) (PEG-PPG) (2,500 g/mol) were supplied by Sigma Aldrich. PLA and PCL pellets were dried in an oven at 40°C for 16 hr prior to the blending process. The blend was prepared by melt mixing using a Barbender internal mixer at 180°C and 50 rpm for 6 min. The blend ratio of PLA/PCL was controlled at 80/20 (w/w), and PEG-PPG was added at 0, 2.5, 5.0, 7.5, and 10 phr. The abbreviation for each sample is assigned as followings: PLA/PCL, PLA/PCL/2.5, PLA/PCL/5.0, PLA/PCL/7.5, and PLA/PCL/10, respectively.

## 2.2. Characterization

Morphology of the blends was observed using a scanning electron microscope (JSM-5410LV, JEOL) with 10kV accelerating voltage. The specimen was sputter-coated with a thin layer of gold prior to examination. Differential scanning calorimetric (DSC) study was carried out using a NETZSCH DSC 204 F1 to evaluate the miscibility of the blends and the influence of the compatibilized concentrations on thermal quantities, such as glass transition ( $T_g$ ), melting ( $T_m$ ), and crystallization ( $T_c$ ) temperatures, and degree of crystallinity. The sample was heated from 30°C to 200°C with a heating rate of 10°C/min (hold at 200°C for 3 min), then cooled to -80°C (hold for 3 min), and secondly heated to 200°C with the same heating rate under a nitrogen atmosphere. Crystallinity of PLA phase in the blends was determined using the following equation [13]:

$$X_{c,PLA}(\%) = \frac{\Delta H_{c,PLA}}{\Delta H_m^0 \times w_{PLA}} \times 100 \quad (1)$$

Where  $\Delta H_{c,PLA}$  is the enthalpy of crystallization of PLA,  $\Delta H_m^0$  is the enthalpy of fusion of PLA crystal having infinite crystal thickness (93 J/g), and  $w_{PLA}$  is the weight fraction of PLA.

All the blended samples were molded by hot-pressing at 180°C to make a sheet of 0.2 mm thickness and cut into a rectangle shape (15 mm width and 50 mm length) for tensile measurement (Universal testing machine, INSTRON 3366). The test was performed with a crosshead speed of 3 mm/min. A minimum of five samples was repeatedly tested and averaged.

## 3. Results and Discussion

### 3.1. Morphology

Morphology of the fractured surfaces was examined by using SEM. The micrographs showed that the PLA/PCL blend was immiscible, in which the PCL phase is noticeably distributed in the PLA matrix as seen in Figure 1(a). When PEG-PPG is added at 7.5 phr in the polymer blends, it is seen that the size distribution of PCL phase is more uniform and better miscible in the PLA matrix than in the uncompatibilized PLA/PCL blend displayed in Figure 1(b). The result suggests that PEG-PPG can improve miscibility between phases. The excess amount of PEG-PPG might potentially dissolve in the PLA matrix as well. Morphologies shown in Figure 1(c), (d) will be later discussed and correlated with the tensile results of the blends in the next section.

### 3.2. Mechanical property

The addition of PCL (at 20%wt) in PLA produces an effective increase in the strain at break, which is higher than that of the neat PLA. Such result indicates that PLA represents a more brittle behavior than the PLA/PCL blend. With increasing concentration of PEG-PPG in the polymer blends, it results in a continuous increasing strain at break as included in Table 1, concurrently accompanied by a decrease in the modulus and maximum strength. PLA/PCL/2.5 and PLA/PCL/5 exhibit approximately 5 times higher than that of the neat PLA/PCL. However, the tensile stress and modulus continue to decrease. The optimal concentration of PEG-PPG is attained at 7.5 phr, where the highest strain is achieved approximately at 74% (about 10 times higher than that of the neat PLA/PCL). At 10 phr, the strain tends

to drop, reaching a compatibilization limitation. It was previously reported that 10% wt of PCL increased the elongation of the blend by 19%, and the elongation was continuously increased with the PCL content till 20% wt, thereafter it got reduced [11]. Na et al. studied compatibility of polymer blends between PLA and PCL, using PCL-b-PEG as a compatibilizer [14]. When PCL-b-PEG was added at 10% wt, it was found that elongation was enhanced by 20%. Because the PEG block copolymer can be nicely compatible with the PLA phase, generating a strong interfacial adhesion between the surfaces of PLA and PCL; thus improving mechanical property of the polymer blends. SEM micrographs of the tensile fractured surfaces of the blends are illustrated in Figure 1(c), (d). It is obviously seen that the dispersed PCL phase is effectively stretched out (Figure 1(c)), corresponding to the strain increment. The presence of PEG-PPG in the blends promotes phase compatibilization, producing an elongated structure in the PLA matrix seen in Figure 1(d). The elongation combined from both PLA and elastomer phases consequently results in a drastic enhancement of strain at break.

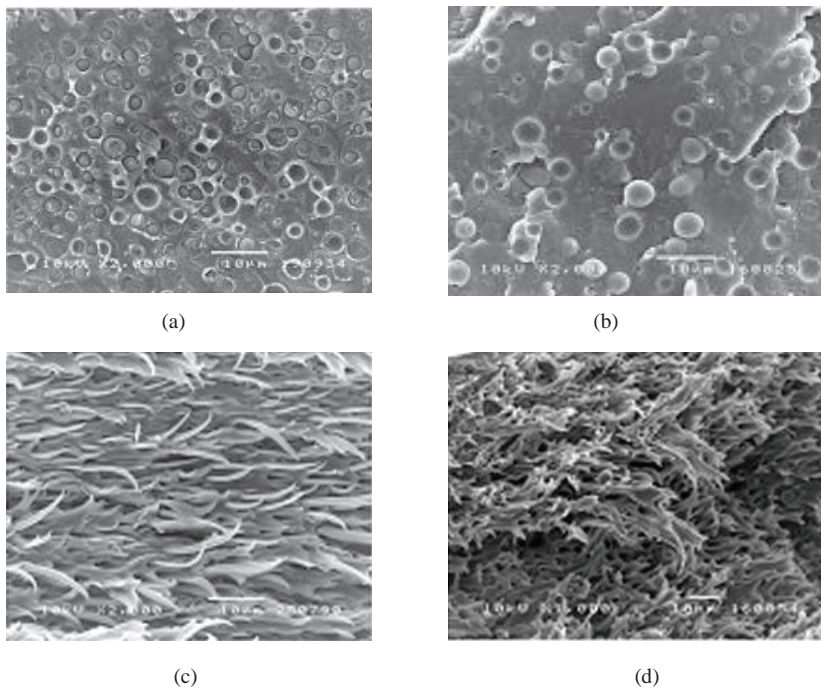


Fig. 1. SEM micrographs of PLA/PCL blends before tensile testing: (a) neat PLA/PCL; (b) PLA/PCL/PEG-PPG7.5, and after tensile testing: (c) neat PLA/PCL; (d) PLA/PCL/PEG-PPG7.5.

Table 1. Maximum stress, strain at break, and modulus of PLA and PLA/PCL blends containing various contents of PEG-PPG

| Samples     | Maximum stress (MPa) | Strain at break (%) | Modulus (GPa) |
|-------------|----------------------|---------------------|---------------|
| PLA         | 51.3                 | 2.2                 | 3.2           |
| PLA/PCL     | 40.4                 | 8.2                 | 2.5           |
| PLA/PCL/2.5 | 31.8                 | 43.7                | 1.9           |
| PLA/PCL/5.0 | 29.5                 | 38.1                | 1.9           |
| PLA/PCL/7.5 | 25.0                 | 74.4                | 1.4           |
| PLA/PCL/10  | 24.8                 | 32.6                | 1.3           |

### 3.3. Thermal property

DSC thermograms of the neat PLA, neat PLA/PCL, and PLA/PCL/PEG-PPG blends with various contents of PEG-PPG are illustrated in Figure 2. The thermogram of PLA exhibits both  $T_g$  and  $T_m$  found at 60°C and 151.9°C, respectively. While the thermogram of PLA/PCL blend displays two distinguished  $T_m$ s, corresponding to PCL (at 52.5°C) and PLA (at 150°C) melting temperatures. In the blends,  $T_g$  of PLA could not be detected since it might overlap with  $T_m$  of PCL. Similarly, Todo et al. reported that a peak around 70°C appeared in the PLLA/PCL blends was recognized as the melting point of PCL [15]. The glass transition of PLLA was present in this region as well. By blending PCL at 20 %wt, it helps increasing %crystallinity of PLA (Table 2). Crystallinity of PLA was evaluated using equation (1). Nam et al. found that the overall crystallization rate of PLA was increased significantly with the addition of *N,N*-ethylenebis(1,2-hydroxystearamide) [16]. Since the additive can serve as a nucleating agent during crystallization stage of PLA. Such effect was also reported for poly(ethylene glycol) (PEG), which could also function as an effective polymeric plasticizer to facilitate the crystallization rate of PLA resins. Li and Huneault found that PEG accelerated crystallization ability of PLA, while cold crystallization temperature of PLA molecules was decreased significantly after the addition of PEG [17]. Consequently, the spherulite growth rate of PLA was simultaneously increased, and the nucleation density was decreased. Likely, PEG-PPG used in this project also induces crystallization in the blends, in which the degree of crystallization is enhanced, while the crystallization temperature ( $T_c$ ) is shifted to lower region (Table 2). By increasing PEG-PPG concentration,  $T_c$  of the blends is continuously declined, while %crystallinity is gradually increased, which is favorable for processing condition. Besides, in the compatibilized blends, a bimodal melting temperature of PLA is observed. This corresponds to the formation of different crystal structures:  $\beta$ -form that melts at lower temperature ( $T_{m1}$ ), and  $\alpha$ -form that melts at higher temperature ( $T_{m2}$ ) [18].

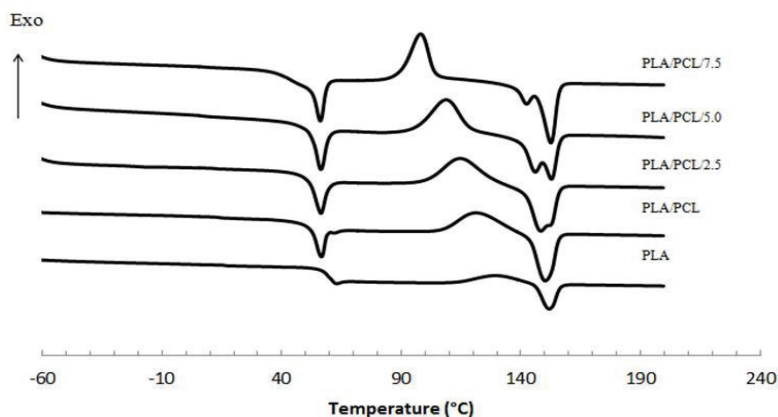


Fig.2. DSC thermograms of PLA and PLA/PCL blends with various concentrations of PEG-PPG.

Table 2. Thermal property of PLA and PLA/PCL blends containing various contents of PEG-PPG (2<sup>nd</sup> heating)

| Samples     | $T_c$ (°C) | $T_m$ (°C) |          | Crystallinity (%) |
|-------------|------------|------------|----------|-------------------|
|             |            | $T_{m1}$   | $T_{m2}$ |                   |
| PLA         | 129.2      | -          | 151.9    | 8.0               |
| PLA/PCL     | 121.2      | -          | 150.0    | 23.8              |
| PLA/PCL/2.5 | 114.4      | 148.4      | 152.0    | 30.4              |
| PLA/PCL/5.0 | 108.8      | 146.0      | 152.7    | 32.5              |
| PLA/PCL/7.5 | 98.1       | 142.3      | 152.5    | 33.5              |

#### 4. Conclusion

The PLA/PCL blends compatibilized with the block copolymer (PEG-PPG) were investigated. SEM micrographs revealed that the PCL phase was better distributed and more miscible in the PLA matrix. Increasing in concentration of PEG-PPG in the blends resulted in a drastic increase in strain at break, in which the optimum was obtained at 7.5 phr, reaching 74% strain. The presence of compatibilizer reduced crystallization temperature and enhanced degree of crystallinity of the blends.

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