

## Miscibility and Crystallization of Poly(L-lactide)/Poly(ethylene glycol) and Poly(L-lactide)/Poly( $\epsilon$ -caprolactone) Blends

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**ABSTRACT:** The miscibility and crystallization behavior of two binary blends, poly(L-lactide) (PLLA)/poly(ethylene glycol) (PEG) and PLLA/poly( $\epsilon$ -caprolactone) (PCL), with PLLA as the main component (PLLA composition was not lower than 50 wt%) have been investigated by differential scanning calorimetry (DSC) and optical microscopy. PEG and PCL with moderate molecular weight ( $MW \approx 10000$ ) were used as the blending components for PLLA. PLLA and PEG were miscible in the melt over the composition range investigated. The variation of the bulk crystallization rate of PLLA with PEG composition displayed a maximum at 10 wt% PEG. On the other hand, a monotonic increase in spherulite growth rate with increasing PEG composition was observed. Since the bulk crystallization rate is determined by both the nucleation density and the growth rate, the depression of nucleation density coupled with the increase of growth rate with increasing PEG composition may give rise to the observed maximum in the composition variation of the bulk crystallization rate. The crystallizability of PLLA and PEG in the blends was also evaluated. The crystallizability of PEG was reduced by blending with PLLA, while that of PLLA was essentially unaffected by blending with PEG. For the PLLA/PCL system, a phase-separated morphology was identified in the melt. However, the crystallization rate of PLLA could be enhanced upon blending with PCL. Since no preferential nucleation at the domain interface was observed, the promotion of PLLA crystallization rate was attributed to its partial miscibility with PCL.

**KEY WORDS** Poly(L-lactide) / Poly(ethylene glycol) / Poly( $\epsilon$ -caprolactone) / Blends / Miscibility / Crystallization Behavior /

Biodegradable polymers have attracted increasing attention due to their potential applications as biomedical and environment-friendly materials. In addition to mechanical and thermal properties, the rate and extent of degradation are the essential considerations for biodegradable polymers. The degradation behavior of biodegradable polymers has been frequently controlled by modifying the chemical or stereochemical compositions of the polymers.<sup>1–5</sup> Copolymerization, for example, is a popular method for such a modification.<sup>1,2,5</sup> Besides the chemical nature, the morphology of a biodegradable polymer may also be an influential factor on its degradation behavior. For example, when a semi-crystalline biodegradable polymer is subjected to a degradation medium such as water and enzyme, the molecules of the medium would enter into the amorphous regions more easily than into the crystalline regions. The degradation rate will then depend on the degree of crystallinity and the chain packing in the amorphous regions, which are determined by the thermal history and the molecular weight. Therefore, morphological controls through thermal history and molecular weight variations, physical aging, and chain orientation may also be useful for controlling the degradation behavior of a biodegradable polymer.

In addition to the aforementioned methods, blending may also serve an effective route for controlling the degradation behavior, since miscibility may affect the

crystallizability and the morphology of biodegradable polymers.<sup>6–18</sup> In the present study, the binary blends of a biodegradable polymer, poly(L-lactide) (PLLA), with a biocompatible polymer, poly(ethylene glycol) (PEG), and with another biodegradable polymer, poly( $\epsilon$ -caprolactone) (PCL), are investigated. PLLA is semi-crystalline with the equilibrium melting point ( $T_m^0$ ) of 215°C and the glass transition temperature ( $T_g$ ) of 60°C.<sup>19</sup> Several blending systems of PLLA have been investigated previously, such as PLLA/poly(ethylene oxide) (PEO),<sup>12,18</sup> PLLA/poly(D-lactide) (PDLLA),<sup>6,9–10</sup> and PLLA/PEO–poly(propylene oxide) (PPO)–PEO triblock copolymers.<sup>11</sup> For the two blend systems reported in this study, PLLA is considered as the main component such that the composition of the other component was not higher than 50 wt%. Besides, PEG and PCL with moderate molecular weights are used as the blending components for PLLA in order to achieve good compatibilities. Since miscibility, crystallizability, and the resultant morphology are the first concerns for the blends, the discussions of this paper will center on these subjects. The *in vitro* degradation studies of these systems are currently underway and will be reported in the future.

### EXPERIMENTAL

PLLA was purchased from Sigma Chemical Company with the reported molecular weight of 85000. PEG and

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PCL were obtained from Aldrich. The molecular weight of PEG and PCL was about 10000 and 15000, respectively.

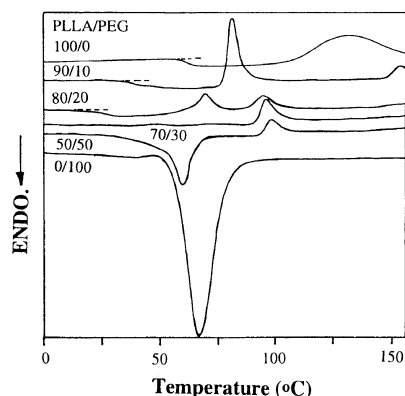
Blendings of PLLA with PEG and PCL were carried out by solution casting. The blending components were dissolved in chloroform at room temperature yielding a 1 wt% solution. The solution was subsequently poured onto a petrie dish and the blend film was obtained after evaporating most chloroform solvent on a hot plate at *ca.* 80°C. The blend film was then further dried *in vacuo* at 60°C for 24 hours.

Thermal analyses of the blends were performed with a TA Instrument 2000 differential scanning calorimeter. For the evaluation of miscibility, the blends were first annealed at 200°C for 3 minutes to erase previous thermal history followed by quenching into liquid nitrogen. The samples were subsequently scanned at 20°C min<sup>-1</sup> to observe the glass transition and the cold crystallization. For evaluating the crystallizability of PLLA, the blends were first annealed at 200°C for 3 minutes followed by quick cooling at *ca.* 70°C min<sup>-1</sup> to the desired crystallization temperature ( $T_c$ , between 125 and 80°C). After crystallization for 5 hours, the samples were quenched to room temperature and the DSC scans were conducted at 20°C min<sup>-1</sup> to observe the melting endotherms of PLLA.

The spherulite growth and morphology were monitored with an Olympus BH-651P polarized optical microscope. The blend was first melted on a Linkam TP92 hot stage at 200°C for 3 minutes. The sample was then quickly transferred to another hot stage equilibrated at 125°C and the spherulite growth or morphology was monitored. Micrographs were taken at intervals for measuring the spherulite radii at various time periods. The growth rate was calculated from the change of spherulite radius with time,  $dR/dt$ .

## RESULTS AND DISCUSSION

Figure 1 shows the DSC thermograms of melt-quenched PLLA/PEG blends. A single  $T_g$  can be identified in the figure for the blends with PEG composition less than 30 wt%. As the scale of the figure was further enlarged, the  $T_g$  of 70/30 composition may also be identified. Figure 2 plots the observed  $T_g$  vs. the



**Figure 1.** DSC thermograms of melt-quenched PLLA/PEG blends. The blends have been annealed at 200°C for 3 min followed by quenching into liquid nitrogen. The melting endotherms of PLLA are not shown in the figure. The scanning rate was 20°C min<sup>-1</sup>.

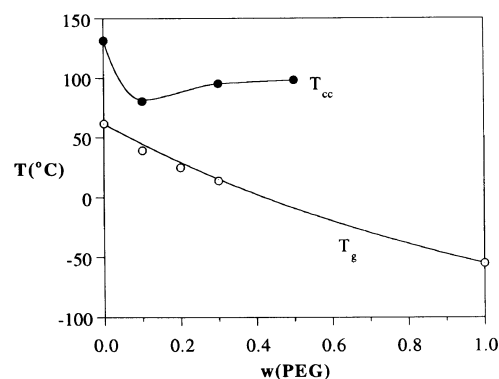
weight fraction of PEG,  $w(\text{PEG})$ . The  $T_g$  drops with increasing PEG composition, showing that PLLA and PEG were miscible in the melt up to at least 30 wt% of PEG. The  $T_g$ -composition variation can be described by the Fox equation:

$$\frac{1}{T_g} = \frac{w(\text{PLLA})}{T_g(\text{PLLA})} + \frac{w(\text{PEG})}{T_g(\text{PEG})} \quad (1)$$

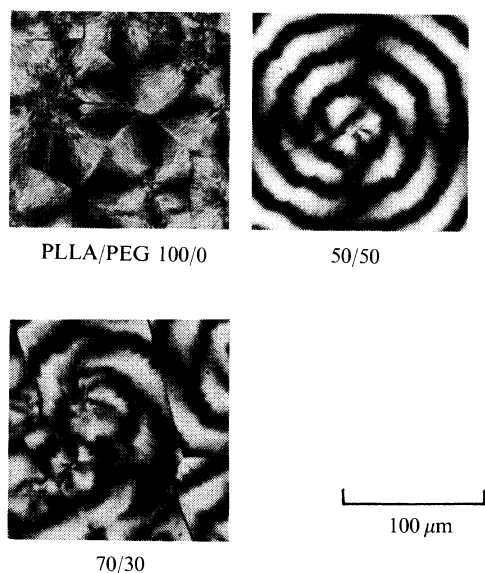
This implies that the intermolecular interaction between PLLA and PEG was not strong.

The effect of blending with PEG on the crystallization rate of PLLA can be evaluated from the locations of the cold crystallization exotherms in Figure 1. It is noted that two exotherms are observed for 80/20 blend. This is due to the overlap between the cold crystallization exotherm of PLLA and the melting endotherm of PEG. The cold crystallization of PLLA occurred in the region where the melting of PEG crystals also took place. The overlap between a crystallization exotherm and a melting endotherm could give rise to two peaks as that shown in Figure 1 (similar to the case where the occurrence of recrystallization in the melting region of a crystalline polymer could lead to multiple melting endotherms). Although such an overlap exists, only one cold crystallization peak is observed for other blend compositions, the peak positions of these exotherms (the cold crystallization temperature,  $T_{cc}$ ) can hence be identified unambiguously. A higher value of  $T_{cc}$  would mean that PLLA crystallized later during the DSC scan and hence indicates a slower crystallization rate. Figure 2 plots  $T_{cc}$  against the blend composition. Because two exotherms were observed for 80/20 blend, the  $T_{cc}$  of this composition is not shown in Figure 2. The  $T_{cc}$  of pure PLLA is seen to be higher than that of the blends, showing that the crystallization rate of PLLA was promoted by the presence of PEG. The variation of  $T_{cc}$  with composition is not monotonic but exhibits a minimum at 10 wt% of PEG. It appears that the crystallization rate of PLLA could be promoted most effectively by blending with 10 wt% of PEG, further increase in PEG composition, although could still enhance the crystallization rate of PLLA, did not provide as effective promotion.

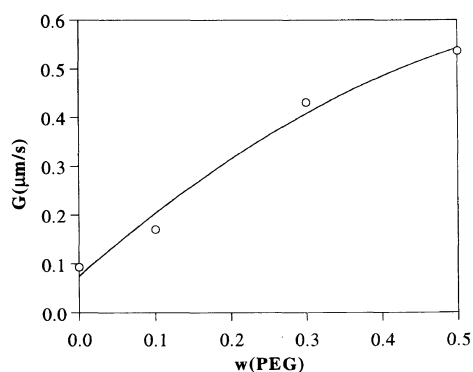
The crystallization kinetics investigated by DSC is the bulk crystallization rate which contains both the nucleation density and growth rate. Therefore, the observed composition variation of PLLA crystallization



**Figure 2.** Composition variations of  $T_g$  and PLLA cold crystallization temperature ( $T_{cc}$ ) of PLLA/PEG blends. The  $T_g$ -composition curve represents the prediction by the Fox equation.



**Figure 3.** Morphology of PLLA spherulites in PLLA/PEG blends. The crystallization temperature was 125°C. The nucleation density was decreased upon blending with PEG. The ringed pattern which did not appear for pure PLLA is observed for the blends.



**Figure 4.** Composition variation of PLLA spherulite growth rate in PLLA/PEG blends. The growth rate increases monotonically with increasing PEG composition. The crystallization temperature was 125°C.

rate might be interpreted if the respective effects of blend composition on the kinetics of nucleation and growth are considered. The composition effect on the nucleation density can be evaluated by comparing the ultimate spherulite size based on the observation by polarized optical microscopy. The composition effect on the growth rate can of course be evaluated by measuring the temporal development of PLLA spherulites. Figure 3 displays the micrographs of PLLA spherulites grown from the pure melt and the blends at 125°C. Since 125°C is higher than the  $T_m^0$  of PEG, only PLLA could crystallize at this temperature. The size of the spherulites is seen to increase with increasing PEG content; thus, blending with PEG has the effect of decreasing the nucleation density of PLLA.

Figure 4 displays the composition variation of growth rate for PLLA/PEG blends at 125°C. In contrast to the nucleation density, the growth rate increases with increasing PEG composition. The monotonic increase of growth rate with PEG composition up to 50 wt% PEG indicates that PLLA and PEG were also miscible in the melt with 50/50 composition. Therefore, it is suggested

that PLLA/PEG blends were miscible over the composition range investigated.

Based on the above observations on the nucleation density and the growth rate, it can be concluded that blending with PEG has exerted two opposing effects on the crystallization kinetics of PLLA; one is to depress the nucleation density of PLLA while the other is to increase the spherulite growth rate. The interplay between these two will determine the bulk crystallization rate and hence a maximum may be generated in the composition variation of bulk crystallization rate, as that displayed in Figure 2. This interpretation agrees qualitatively with the experimental observation. However, whether the maximum crystallization rate occurs at 90/10 composition would require further quantitative evaluations of the bulk crystallization rate constant (through Avrami analysis), nucleation density, and growth rate for various PLLA/PEG compositions. This study is currently underway.

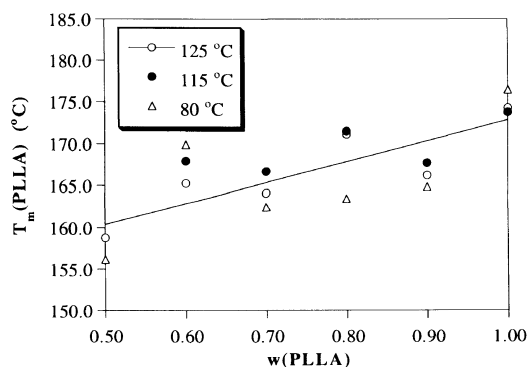
The increase of spherulite growth rate upon blending with PEG is normal in view of the lower  $T_g$  of PEG which would act as a diluent to promote the segmental mobility associated with crystallization for PLLA. On the other hand, the depression of nucleation density of PLLA is quite interesting. Over the past, most attention has been paid to the blending effect on either the bulk crystallization kinetics or the spherulitic growth kinetics, little effort has been made to correlate the miscibility with the nucleation density. The average size of spherulites or the nucleation density is determined by the competition between the rates of nucleation and subsequent growth of the spherulites. The faster the nucleation, the smaller the spherulites will be formed after impingement and thus the higher the nucleation density will be observed. Both the nucleation and growth rates are determined by a mobility term and a term associated with the thermodynamic driving force. The segmental mobility associated with these two events should not be very different; therefore, the difference between the rates of these two processes can be revealed by comparing their respective thermodynamic driving force. For the sake of simplicity, if the nucleation is approximated as a homogeneous primary nucleation, the rate of nucleation of the blend can then be written as<sup>24</sup>

$$i \propto \exp \left\{ - \frac{32\sigma^2\sigma_e T_{mb}^0{}^2}{k_B T_c \Delta h_f^0{}^2 [T_{mb}^0 - T_c]^2} \right\} \quad (2)$$

where  $\sigma$  and  $\sigma_e$  are the side and fold surface free energy, respectively,  $\Delta h_f^0$  is the bulk enthalpy of melting, and  $T_{mb}^0$  is the equilibrium melting point of the blend and  $(T_{mb}^0 - T_c)$  represents the degree of supercooling. On the other hand, the growth rate can be written as<sup>25</sup>

$$G \propto \exp \left\{ - \frac{2\sigma\sigma_e b_0 T_{mb}^0}{k_B T_c \Delta h_f^0 [T_{mb}^0 - T_c]} \right\} \quad (3)$$

Comparing eq 2 and 3, it can be seen that the primary nucleation rate varies with  $\exp[-1/(T_m^0 - T_c)^2]$  while the growth rate varies with  $\exp[-1/(T_m^0 - T_c)]$ . This means that the primary nucleation rate is more susceptible to the change in degree of supercooling than the growth rate. Therefore, a perturbation in degree of supercooling will bring about a greater change in the nucleation rate

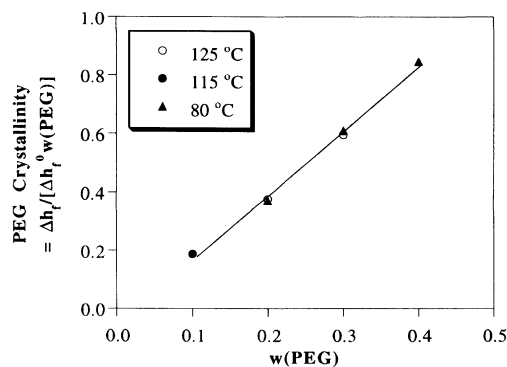


**Figure 5.** Composition variation of the melting points of PLLA in PLLA/PEG blends. The corresponding  $T_c$ s are indicated in the figure. The melting point basically increases with increasing PLLA composition, but no systematic variation of melting points with  $T_c$  can be identified.

than in the growth rate. The study of the molecular weight (MW) effect on the nucleation density of PCL has showed that increasing  $T_m^0$  due to the increase in MW has promoted the nucleation rate in a much more significant fashion than its effect on the growth rate. As a consequence, the nucleation density increases drastically with increasing MW.<sup>26</sup>

For a given  $T_c$ , blending may actually lower the degree of supercooling because of the depression of  $T_{mb}^0$  associated with the miscibility. A slight depression in  $T_{mb}^0$  is expected to induce a strong depression in nucleation rate due to the amplification by the exponential factor. Therefore, the nucleation density of PLLA decreases with increasing PEG composition. Attempt was made to evaluate the depression of  $T_{mb}^0$  of PLLA upon blending with PEG. Since  $T_{mb}^0$  may be extrapolated by the Hoffman–Weeks plot, the melting points of PLLA after crystallizing at 125 to 80°C for 5 hours were measured. Figure 5 plots the measured melting points against the weight fraction of PLLA. The melting point basically increases with increasing PLLA composition, but no systematic variation of melting point with  $T_c$  can be identified. This may be ascribed to the occurrence of crystal reorganization during the DSC scans. Since polymer crystals are metastable, they may reorganize upon heating to temperatures higher than their  $T_c$ . The observed melting points of PLLA may be the melting point of the reorganized crystals rather than that of the crystals formed prior to the DSC scans.

It is noted in Figure 3 that the after blending with PEG, the spherulites of PLLA exhibited different morphology from that of pure PLLA. The ringed spherulites, which are not observed for pure PLLA, is identified for the blends. The periodicity of the ring is about 25  $\mu\text{m}$ . The spherulitic ringed pattern has also been reported for poly(vinyl chloride) (PVC)/poly( $\epsilon$ -caprolactone) (PCL)<sup>20</sup> and poly(vinylidene fluoride) (PVF<sub>2</sub>)/poly(methyl methacrylate) (PMMA) blends,<sup>21,22</sup> while such a pattern did not appear for the pure crystalline component of these blends. Because the ringed pattern is associated with the spatial twisting of lamellae, the appearance of such a pattern in PLLA/PEG blends may indicate that the presence of PEG has altered the aggregation and twistings of PLLA lamellae. This is likely to occur when PEG was predominantly trapped in the PLLA interlamellar

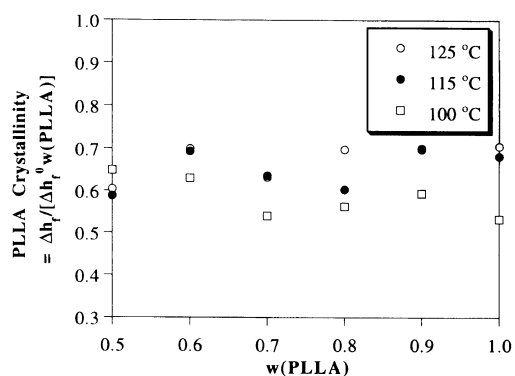


**Figure 6.** Composition variation of the normalized degree of crystallinity of PEG. PLLA/PEG blends were first crystallized at a  $T_c$  indicated in the figure followed by quenching to room temperature and the DSC scans were then conducted. The crystallinity of PEG was presumably developed during the quench. The crystallizability of PEG is seen to decrease with decreasing PEG composition.

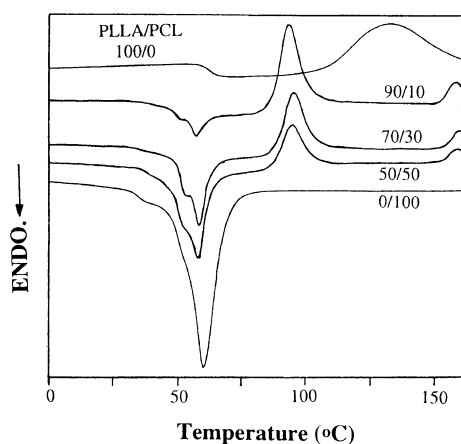
regions after PLLA crystallized. The segregation of PVC into the interlamellar regions upon crystallization of PCL has been observed for PVC/PCL blends which displayed spherulitic ringed pattern.<sup>23</sup>

In this study, we have considered primarily the effect of blending with PEG on the crystallization behavior of PLLA, and hence we mainly concern with a crystalline/amorphous blend system. When PLLA/PEG blends are cooled to the temperature below the melting point ( $<60^\circ\text{C}$ ) of PEG, both PLLA and PEG could crystallize, and the blend would turn into a crystalline/crystalline system whose behavior is more complicated than the crystalline/amorphous system. For example, if PLLA is first allowed to crystallize from the blends at 125°C followed by cooling to 35°C to allow PEG to crystallize, then the crystallization rate of PEG may be reduced or promoted. Since PEG is trapped between the PLLA lamellae, the space available for PEG crystallization becomes more limited which would consequently reduce the crystallization rate of PEG. On the other hand, if the existing PLLA crystals act as the nucleation sites where PEG could nucleate preferentially on the crystal surface, then the crystallization rate of PEG could be increased. Since the investigation on crystalline/crystalline blends is quite limited, PLLA/PEG blends appears to be an interesting system for such a study.

The effect of blending on the crystallizability of PLLA and PEG was also evaluated. PLLA/PEG blends were crystallized at a  $T_c$  for 5 hours followed by quenching to room temperature and the DSC scans of the crystalline blends were conducted. Because of the quenching process, PEG could crystallize prior to the DSC scans; therefore, the melting endotherms of both PEG and PLLA were observed. Figure 6 displays the composition variation of the normalized crystallinity of PEG. The crystallinity was calculated by the enthalpy of melting taking 197  $\text{J g}^{-1}$  as the enthalpy of melting of 100% crystalline PEG. The calculated crystallinity was then normalized by the weight fraction of PEG to signify the crystallinity per gram of PEG. The crystallinity is seen to decrease with decreasing PEG content in the blends. This indicates that the crystallizability of PEG was reduced upon blending with PLLA. The reduction in crystallizability may be associated with the reduction of



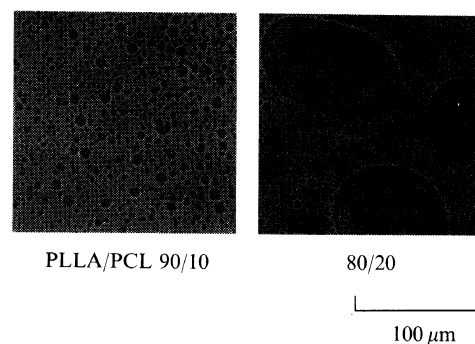
**Figure 7.** Composition variation of the normalized degree of crystallinity of PLLA. The corresponding  $T_c$ s are indicated in the figure. The crystallizability of PLLA was essentially unaffected by blending with PEG.



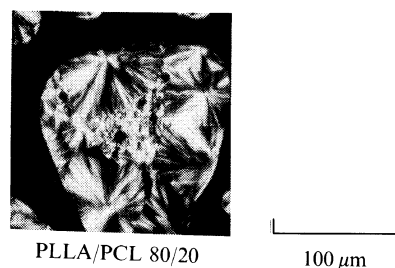
**Figure 8.** DSC thermograms of melt-quenched PLLA/PCL blends. The blends have been annealed at 200°C for 3 min followed by quenching into liquid nitrogen. The melting endotherms of PLLA are not shown in the figure. The scanning rate was 20°C min<sup>-1</sup>.

PEG molecular mobility due to its miscibility with PLLA. Figure 7 displays the composition variation of the normalized crystallinity of PLLA calculated by taking 93.7 J g<sup>-1</sup> as the enthalpy of melting of 100% crystalline PLLA.<sup>27</sup> The crystallinity stays roughly constant with composition, indicating that the crystallizability of PLLA was essentially unaffected by blending with PEG.

In addition to PLLA/PEG system, the blends of PLLA with PCL was also studied. Figure 8 displays the DSC scans of the melt-quenched PLLA/PCL blends. The glass transition region of PLLA overlaps significantly with the melting range of PCL; therefore, the  $T_g$  of the blends cannot be identified directly from the thermograms if these two polymers are miscible. Nevertheless, the cold crystallization exotherms of PLLA may provide some information on the miscibility. A cold crystallization exotherm located at 131°C is observed for pure PLLA. This exotherm shifts to 95°C upon blending with 10 wt% of PCL, but further increase in PCL composition does not change the position of this exotherm. Similar to PLLA/PEG system, the crystallization rate of PLLA could be promoted considerably with the addition of 10 wt% PCL; but in contrast to PLLA/PEG, the crystallization rate of PLLA was not altered by further increase of PCL composition. If PLLA is miscible with PCL over the composition range investigated, the pres-



**Figure 9.** Morphology of PLLA/PCL 90/10 and 80/20 blends at 200°C.



**Figure 10.** Morphology of PLLA/PCL 80/20 blend after cooling from 200 to 115°C. PLLA spherulites were formed but no preferential nucleation at the domain interface was observed.

ence of the lower  $T_g$  PCL may enhance the segmental mobility of PLLA and hence promote the crystallization rate of PLLA. However, in such a case the crystallization rate of PLLA should increase monotonically or exhibit a maximum as for PLLA/PEG blends with increasing PCL composition. On the other hand, if PLLA and PCL are not miscible, the interface of the phase-separated domains may provide the favorable nucleation sites for crystallization,<sup>28</sup> and thus the crystallization rate of PLLA may also be promoted due to a lower nucleation barrier compared with the nucleation of PLLA from the pure bulk melt.

In order to judge the miscibility between PLLA and PCL and to see whether the favorable nucleation at the domain interface has taken place if these two polymers are not miscible, the study by optical microscopy was conducted. Figure 9 shows the morphology of PLLA/PCL 90/10 and 80/20 blends at 200°C. It is apparent that phase-separated morphology was formed, indicating that these two polymers were not fully miscible in the melt. Figure 10 presents the morphology of 80/20 blends after cooling from 200°C to 115°C. PLLA spherulites were formed but the nucleation of these spherulites did not seem to take place favorably at the domain interface. Figure 9 and 10 have shown neither the miscibility between PLLA and PCL in the melt nor the occurrence of favorable nucleation at the domain interface. Therefore, the promotion of PLLA crystallization rate upon blending with PCL is attributed to the partial miscibility of these two polymers. As PLLA and PCL were partially miscible in the melt, the slight amount of PCL in the PLLA-rich domains may promote the crystallization rate of PLLA. Because the composition of PCL in the PLLA-rich domains was independent of the overall PCL composition as prescribed by the phase

diagram, the crystallization rate of PLLA in the blends was relatively independent of composition.

### CONCLUSION

The miscibility and crystallization of PLLA/PEG and PLLA/PCL blends with PLLA as the main component have been investigated. PLLA and PEG were miscible in the melt over the composition range investigated. The miscibility promoted the spherulite growth rate but depressed the nucleation density of PLLA. The interplay between these two effects generated a maximum in the composition variation of the bulk crystallization rate of PLLA. The bulk crystallization rate of PLLA was promoted most effectively upon blending with 10 wt% of PEG. The crystallizability of PEG was decreased by blending with PLLA, while that of PLLA was not affected noticeably upon blending with PEG. Phase-separated morphology was identified for PLLA/PCL blends. Although this binary system exhibited phase separation in the melt, the crystallization rate of PLLA could be enhanced by blending with PCL. The partial miscibility of these two polymers was suggested to cause the promotion in crystallization rate.

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