

Effect of P(*l*/LA-*co*- ϵ CL) on the Compatibility and Crystallization Behavior of PCL/PLLA Blends

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ABSTRACT: This article describes the compatibility of two semicrystalline polymers, poly(ϵ -caprolactone) (PCL) and poly(*l*-lactic acid) (PLLA). The compatibility of the PCL/PLLA blends was enhanced by the compatibilizing effect of the poly(*l*,*l*-lactide-*co*- ϵ -caprolactone) [P(*l*/LA-*co*- ϵ CL)]. A discussion details the effect of the concentration of the compatibilizing agent, the copolymer of *l*,*l*-lactide and ϵ -caprolactone of a 50/50 mol ratio [P(*l*/LA-*co*- ϵ CL)], on the compatibility and the crystallization behavior of the blends of PCL and PLLA. It was found that the addition of P(*l*/LA-*co*- ϵ CL) could suppress the crystallization of PLLA at its T_c and induced the concurrent crystallization of PLLA and PCL. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 226–231, 2000

Key words: polycaprolactone; poly(*l*-lactic acid); P(*l*/LA-*co*- ϵ CL); crystallinity; concurrent crystallization

INTRODUCTION

Biodegradable polymers have attracted increasing attention owing to their potential applications as biomedical and environment-friendly materials. Aliphatic polyesters derived from glycolic acid, *d*,*l*- and *l*-lactic acid, β -hydroxybutyrate, and ϵ -caprolactone have been most importantly considered as biodegradable polymers. These have found frequent applications as biodegradable matrices for prosthetics and controlled drug delivery.^{1–3} Among them, polylactides (PLA) and poly(ϵ -caprolactone) (PCL) are well known for their nontoxicity, biocompatibility, biodegradability, and permeability. PLA has been reported to possess fast hydrolysis but with low permeability. On the contrary, PCL

shows good permeability but it biodegrades very slowly.^{4–7} To combine the good permeability of PCL with the fast biodegradation of PLA for controlling the degradation rate and the drug-release rate, copolymerization or blending techniques have been applied.

Copolymerization is known to be a popular method for obtaining the proper properties of the biodegradable polymers through the change of the chemical nature or morphology. Random and block copolymers of lactide and ϵ -caprolactone have been utilized for regulating the degradation rate, mechanical properties, and drug-release profiles.^{5–12} Besides the copolymerization method, blending could also serve as an effective route for controlling the properties of the biodegradable polymers. Several blend systems of the blend pairs of poly(*l*-lactide) (PLLA), poly(*d*-lactide) (PDLA), or poly(*d*,*l*-lactide) (PDLLA) with poly(ϵ -caprolactone) (PCL) have been investigated previously.^{1,13–15} In the blends, the compatibility between the components in the blend will usually play an important role in the determination of the properties of the blended polymers. A few studies have

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reported that the high molecular weight PCL and PLLA in the blend are immiscible.^{1,14,15}

In this article, we report on the compatibility enhancement of the high molecular weight PCL/PLLA blend. The copolymer of *l,l*-lactide and ϵ -caprolactone of a 50/50 mol ratio, poly(*l,l*-lactide-co- ϵ -caprolactone) [P(LA-co- ϵ CL)], was used as a compatibilizer to enhance the compatibility between PCL and PLLA in the blend. The effect of the compatibilizer on the crystallization behavior of the PCL/PLLA blend system was also investigated.

EXPERIMENTAL

Materials and Blends Preparation

PLLA ($\bar{M}_w = 200,000$) and PCL ($\bar{M}_w = 170,000$) were purchased from Polyscience (Los Angeles, CA) and Union Carbide (Danbury, CT), respectively. The copolymer, P(LA-co- ϵ CL) ($\bar{M}_w = 51,000$), was synthesized by ring-opening polymerization using stannous octoate as a catalyst and characterized in the same way as in our previous study.⁸ The composition of the P(LA-co- ϵ CL) used in this work was *l,l*-lactide/ ϵ CL = 50/50 on a molar basis. The average number of sequential comonomer units of *l*LA and ϵ CL unit per P(LA-co- ϵ CL) chain were 3.4 and 2.0, respectively, which were determined from the ¹³C-NMR spectra of P(LA-co- ϵ CL).

The blend films were prepared by a solution-casting method using methylene chloride as a solvent. Methylene chloride solutions having different PCL, PLLA, and P(LA-co- ϵ CL) contents were prepared at a total polymer concentration of 4 wt % and then cast onto the flat glass plates, followed by solvent evaporation at room temperature for 1 day. The resulting films were dried in a vacuum for 1 day to ensure complete removal of the solvent at room temperature.

DSC Measurement

Thermal analysis of the blends was performed with a differential scanning calorimetry apparatus (DuPont TA 2000) calibrated with indium ($T_m = 156.6^\circ\text{C}$) to obtain the melting point, the heat of fusion, and the crystallization temperature for the PCL/PLLA blends. For investigation of the crystallinity of PCL in the PCL/PLLA blend, each sample was scanned from -100 to 200°C by heating at a rate of $10^\circ\text{C}/\text{min}$ under a nitrogen atmo-

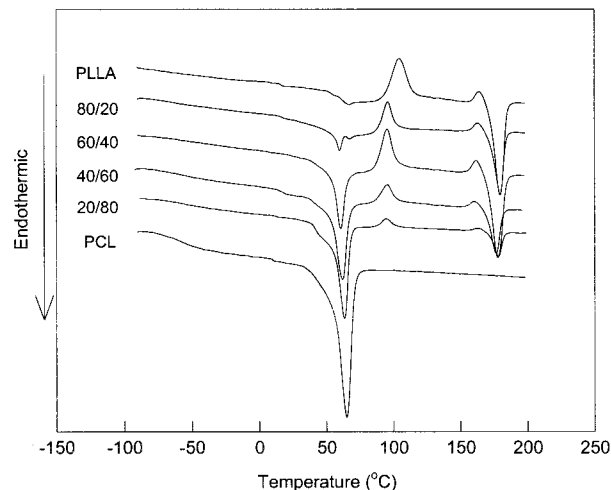


Figure 1 DSC heating thermograms of noncompatibilized PCL/PLLA blends.

sphere. From the heating curves, the crystallinity of PCL could be obtained by calculating the heat of fusion of PCL.

Optical Microscopy

For polarized microscopy, a Leitz polarizing microscope (LABORLUX 12POL) equipped with a 35-mm camera was used. The crystalline structure of PCL in the blends with various contents of the compatibilizer was observed by taking optical micrographs ($\times 500$) of the solvent-cast film of the blend at room temperature.

RESULTS AND DISCUSSION

Compatibility of PCL/PLLA Blend With and Without Containing P(LA-co- ϵ CL)

To investigate the compatibility of PCL and PLLA, the DSC thermograms of the PCL/PLLA blends without containing a compatibilizer were obtained and the results are shown in Figure 1. It was found that the glass transition region of PLLA overlaps significantly with the melting range of PCL and, thus, the T_g of PLLA in the blends could hardly be identified directly from the thermograms. However, a recrystallization exotherm of PLLA in the blend could provide some information on the miscibility of the blend. The recrystallization peak for pure PLLA was observed at 104°C . It shifted to 95°C upon blending with 20 wt % of PCL, but further increase of the PCL content in the blend did not change the po-

sition of the crystallization peak. It means that the recrystallization of PLLA could be more easily induced with the addition of 20 wt % PCL, but was not significantly altered by further increase of the PCL content. This phenomenon is similar to the previous result of Yang et al.¹⁵ on the compatibility of the PCL/PLLA blend. They interpreted their results as follows: If PLLA is miscible with PCL over the composition range investigated, the presence of PCL with the lower T_g may enhance the segmental mobility of PLLA and, hence, promote the recrystallization of PLLA in the blend. In such a case, the recrystallization of PLLA will be enhanced by increasing the PCL content. However, if the two components in this blend are only partially miscible, only a limited amount of PCL will be in the PLLA-rich domains. In that case, the composition of PCL in the PLLA-rich domains will be independent of the overall PCL composition. The recrystallization of PLLA in the blends would thus be relatively independent of composition.

To enhance the compatibility of the PCL/PLLA blend, we introduced the copolymer, P(/LA-co- ϵ CL), as a compatibilizer for the blend of PCL/PLLA. Figure 2 shows the DSC thermograms of the PCL/PLLA blends with a composition of 50/50 in weight compatibilized with P(/LA-co- ϵ CL). The P(/LA-co- ϵ CL) content in the blend was changed from 0 to 20 phr. It is found from Figure 2 that a recrystallization peak of PLLA in the blend shifts to lower temperature as the P(/LA-co- ϵ CL) content increases. It indicates that the addition of

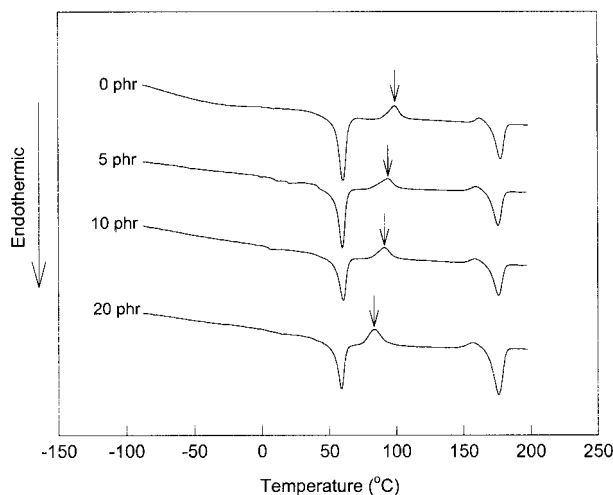


Figure 2 DSC heating thermograms of the PCL/PLLA (50/50) blends with various amounts of P(/LA-co- ϵ CL).

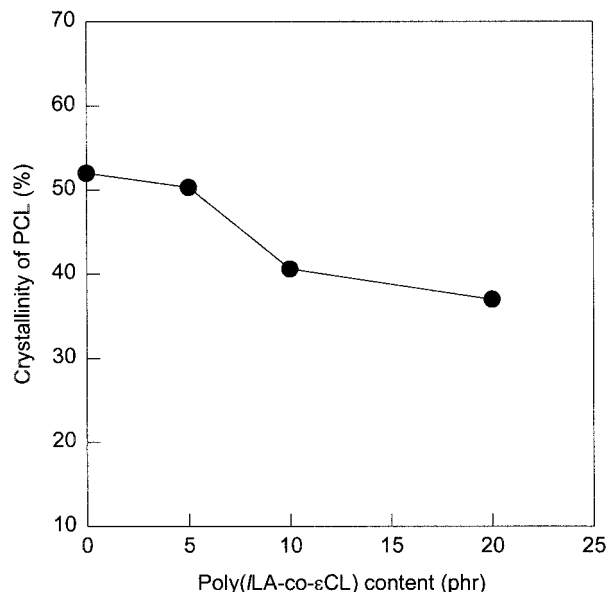


Figure 3 Crystallinity change of PCL in the PCL/PLLA (50/50) blends compatibilized with various amount of P(/LA-co- ϵ CL).

P(/LA-co- ϵ CL) enhances the recrystallization of PLLA by increasing the segmental mobility of PLLA, which represents the compatibility enhancement of the PCL/PLLA blend.

The crystallinity of PCL in the PCL/PLLA blends as a function of P(/LA-co- ϵ CL) content is shown in Figure 3. The crystallinity of PCL in the blend decreases with increase of the P(/LA-co- ϵ CL) content. It indicates that the added P(/LA-co- ϵ CL) is compatible with PCL and thus inhibits the crystallization of PCL in the blend. The compatibility enhancement of the blend can also be evidenced by polarized microscopy. The polarized micrographs of the PCL/PLLA blends with different P(/LA-co- ϵ CL) content are shown in Figure 4. All micrographs shown in Figure 4 were observed with the casts on the slide glass. When the pure PLLA was cast on the glass, no spherulites were observed, since the evaporation of the solvent, methylene chloride, is too fast to crystallize PLLA. Thus, it is confirmed that the spherulites observed in Figure 4 originated from the PCL crystals in the blend. The size of the spherulites is also found to decrease with increase of the P(/LA-co- ϵ CL) content in the blend. This result is consistent with the one shown in Figure 3 that the PCL crystallization is hindered by the presence of the P(/LA-co- ϵ CL) copolymer in the blend. From these results, it is concluded that P(/LA-co- ϵ CL) is compatible with both PCL and PLLA in the

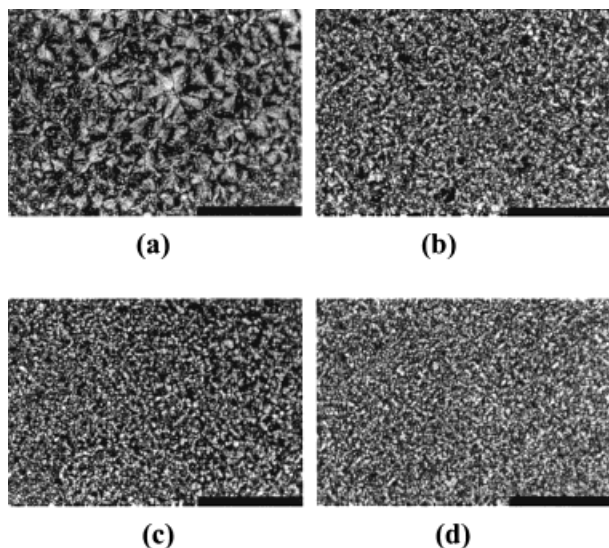


Figure 4 Optical micrographs of PCL/PLLA (50/50) blends which were cast on glass plates under a crossed polarizer: (a) 0 phr P(LA-co-εCL); (b) 5 phr P(LA-co-εCL); (c) 10 phr P(LA-co-εCL); (d) 20 phr P(LA-co-εCL).

blends, which means that P(LA-co-εCL) can be a good compatibilizer for the PCL/PLLA blend.

Crystallization Behavior of PCL and PLLA from the Melt of PCL/PLLA Blend Compatibilized with P(LA-co-εCL)

To investigate the crystallization behavior of the melt of the PCL/PLLA blends, each sample was scanned from 200 to 0°C by cooling at a rate of 2°C/min under a nitrogen atmosphere. From the cooling curves, we could determine the crystallization temperature and the heat of crystallization for the blends. The crystallization thermograms of the PCL/PLLA (50/50) blends compatibilized with various amount of P(LA-co-εCL) are shown in Figure 5. The peak temperature of an exotherm for PCL in the blend does not change significantly with the addition of P(LA-co-εCL) and stays at an almost constant temperature of about 35°C. However, the addition of P(LA-co-εCL) causes a decrease in the peak temperature of an exotherm for PLLA in the blend. The usual peak temperature for the crystallization exotherm of PLLA in the blend with 20 phr P(LA-co-εCL) content was shifted to lower temperature (109°C) from 115°C for PLLA in the noncompatibilized blend. It was also found that the addition of the compatibilizing agent to the PCL/PLLA blend reduces the area of

each crystallization peak of PLLA. As the concentration of P(LA-co-εCL) increases in the blend, the amount of P(LA-co-εCL) located in the PLLA phases increases and retards the crystallization of PLLA and reduces the crystallization temperature of PLLA.

The dependence of the heat of crystallization (ΔH_c) for both PCL and PLLA on the concentration of P(LA-co-εCL) in the blend is plotted in Figure 6. The heat of crystallization at a cooling rate of 2°C/min is about 42 J/g for PCL and about 28 J/g for PLLA in the noncompatibilized PCL/PLLA(50/50) blend. With increasing the amount of P(LA-co-εCL) up to 20 phr, the area of the crystallization peak of PCL increases, whereas that of PLLA decreases. These can be caused by the two discrete steps for the crystallization process of PLLA in the blend: The first step is associated with the higher crystallization temperature for PLLA itself and the second step is associated with the coincident crystallization of PLLA at the crystallization temperature of PCL in the blend. The crystallization of PLLA at the crystallization temperature of PCL does not mean that PLLA cocrystallizes with PCL, since each component shows separate melting endotherms as shown in Figure 7, which represents the heating curves (10°C/min) of the crystallized PCL/PLLA blend. The coincident crystallization of PLLA with PCL in the blend is thus expected to be a

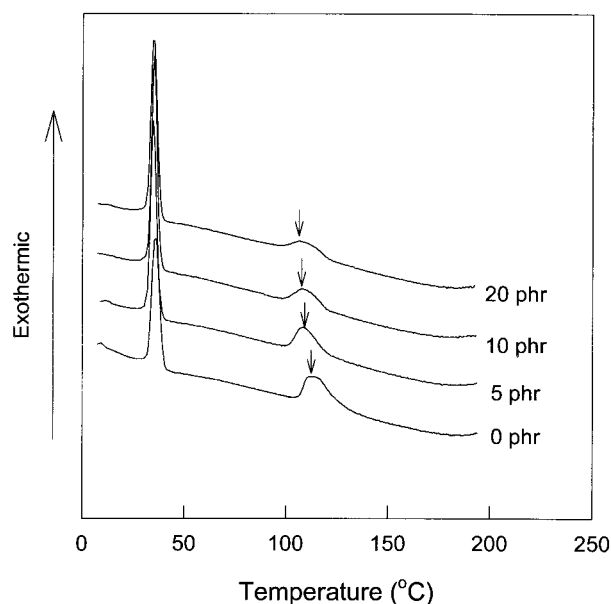


Figure 5 DSC cooling thermograms of PCL/PLLA (50/50) blends with various amounts of P(LA-co-εCL). Cooling rate: 2°C/min.

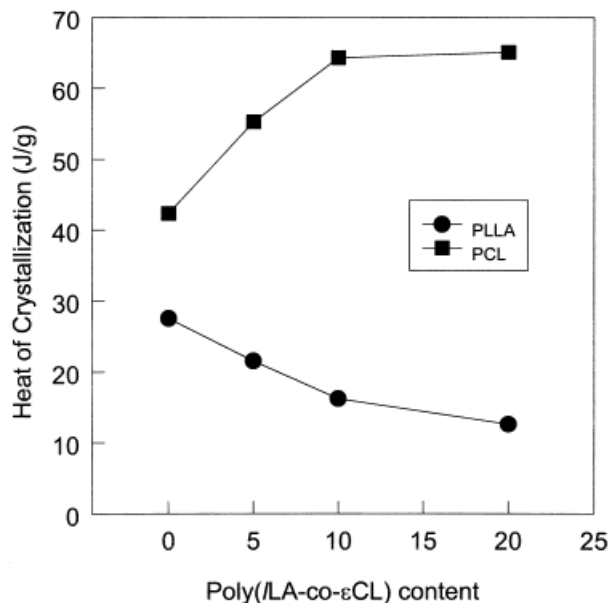


Figure 6 Plot of heat of crystallization (ΔH_c) versus P(LA-co- ϵ CL) content for both PCL and PLLA in PCL/PLLA (50/50) blends.

concurrent crystallization. This kind of concurrent crystallization has been shown in our works on a polypropylene/Nylon-6 blend compatibilized with maleic anhydride-grafted polypropylene.¹⁶ The addition of the small amount of maleic anhydride-grafted polypropylene induced the decrease of ΔH_c for Nylon-6 and the increase of ΔH_c for polypropylene. Similar phenomena have also been reported by others.^{16–19} The concurrent crystallization of

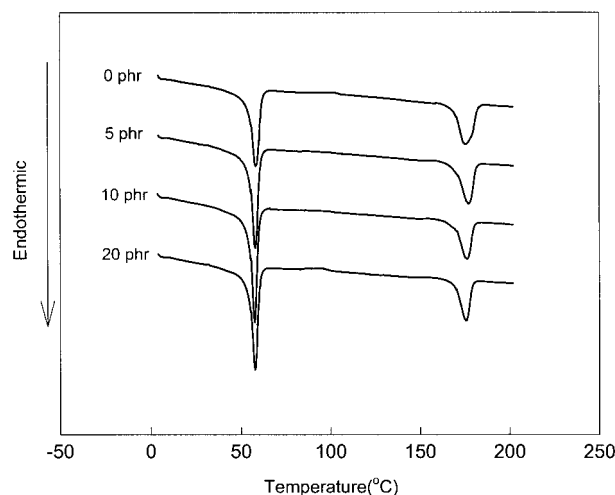


Figure 7 DSC second heating thermograms of PCL/PLLA = 5/5 blends with various amount of P(LA-co- ϵ CL). Heating rate: 10°C/min.

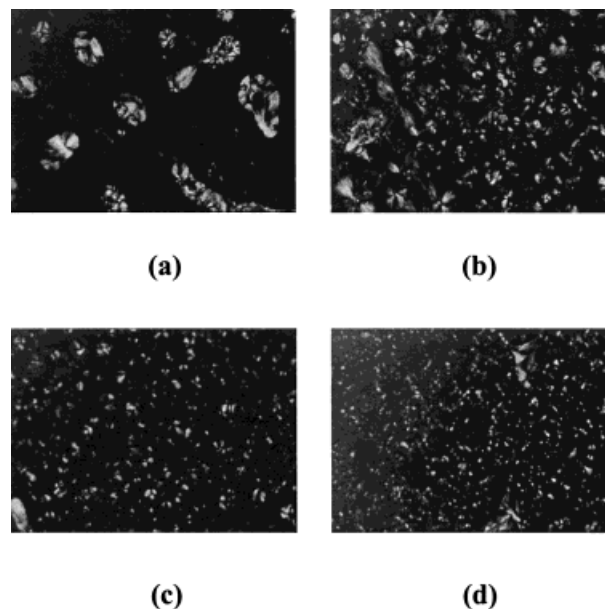


Figure 8 Optical micrographs of PCL/PLLA (50/50) blends that were taken at 100°C under crossed polarizers: (a) 0 phr P(LA-co- ϵ CL); (b) 5 phr P(LA-co- ϵ CL); (c) 10 phr P(LA-co- ϵ CL); (d) 20 phr P(LA-co- ϵ CL).

PLLA with PCL in the blend is thought to be due mainly to the reduction of the particle size of PLLA with increasing concentration of P(LA-co- ϵ CL) in the PCL/PLLA blend. Frensch et al.¹⁷ suggested that as the particle becomes larger the probability for the blend to contain the units of a certain heterogeneity is greater, and, subsequently, the probability to crystallize at its usual crystallization temperature becomes higher.

The concurrent crystallization phenomenon is confirmed by the observation of the optical micrographs under crossed polarizers as shown in Figure 8. Each blend film was heated from room temperature to about 200°C, at which its complete melting was observed, held at that temperature for 2 min, and subsequently cooled at a rate of about 2°C/min to 100°C. At that temperature, the crystalline structure of PLLA in the blends with various contents of the compatibilizer was observed using a magnification of $\times 500$. As the concentration of P(LA-co- ϵ CL) increases, the domain size of the PLLA crystal is found to decrease, and the amount of PLLA crystallized at its usual crystallization temperature decreases, which is in agreement with the DSC results discussed previously.

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