Polymer/Polymer Inclusion Compounds as a Novel Approach To Obtaining a PLLA/PCL Intimately Compatible Blend

Cristian C. Rusa[†] and Alan E. Tonelli*

Fiber and Polymer Science Program, North Carolina State University, P.O. Box 8301, Raleigh, North Carolina 27695-8301

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Introduction. Aliphatic polyesters represent an important family of biodegradable materials. Increasing attention has been focused on hydrolytically unstable lactone polymers owing to their usefulness in biomedical applications.

To enhance the rate of biodegradation, the permeability and the tensile properties of the biomaterials, copolymerization, and blending processes have been used. Blending with other biodegradable polymers might offer a more cost-effective way of modifying the properties of hard and brittle poly(L-lactic acid) (PLLA) than chemical modification.[1,2] Previously, several blend systems containing PLLA have been investigated, such as PLLA/poly(ethylene oxide) (PEO),[3,4] PLLA/poly(DL-lactide) (PDLLA),[5−7] PLLA/PEO−poly(propylene oxide)−PEO copolymers,[8] PLLA/poly(3-hydroxybutyrate) (PHB),[9] PLLA/poly(ϵ-caprolactone) (PCL),[9] and PLLA/poly(*p*-vinylphenol) PVPh.[10] However, most of the blends were found to be immiscible, including a phase-separated morphology identified for PLLA/PCL blends.[9]

Taking advantage of the ability of α-cyclodextrin (α-CD) to form inclusion compounds (ICs) with both PLLA and PCL, an intimately compatible blend can be achieved when PLLA/PCL−α-CD IC was obtained and afterward washed with a solvent (H_2O) for the α-CD host, which is a nonsolvent for the guest polymers.

Recently, we have reported that α-CD forms a crystalline IC with high molecular weight PCL.[11] Here, we have also found that α-CD can form complexes with PLLA (M_w = 285 000), as well as simultaneously with PLLA and PCL.

The miscibility of the PLLA/PCL blend extracted from α-CD IC channels has been investigated by differential scanning calorimetry (DSC), Fourier transform infrared spectroscopy (FTIR), and polarizing optical microscopy. These preliminary results are compared to those of a PLLA/PCL blend cast from their common solution in dioxane.

Experimental Section. a. α-CD IC Formation. A heated solution (50 °C) of PCL (0.4 g, 3.5 mmol in monomer unit, M_w = 65 000) and PLLA (0.25 g, 3.5 mmol in monomer unit, M_w = 285 000) in dioxane (200 mL) was slowly added to 50 mL of an aqueous solution saturated with α-CD (7.25 g, 7.5 mmol) also held at 50 °C. After 1 h of stirring at 50 °C, the solution was allowed to cool to room temperature while continuously stirring for another 24 h. A white powder was collected by filtration and then washed with water and acetone to remove uncomplexed α-CD and free polymers, respectively. The crystals were dried at 90 °C for 24 h. The same procedure was applied for both PLLA−α-CD IC (7 mmol of monomer unit PLLA to 3.5 mmol of α-CD) and PCL−α-CD IC (3.5 mmol of PCL to 3.5 mmol of α-CD) formation. All of the above IC crystals were dissolved in an excess of water (50 °C) under continuously stirring in order to disrupt them. PLLA/PCL−α-CD IC crystals were directly washed with water (50 °C) in a glass Buchner funnel under the effect of vacuum, and a thin film of the coalesced PLLA/PCL blend was obtained. The polymer blend coalesced from its α-CD IC is compared with that obtained by the traditional solution-casting method. PCL, PLLA, and PLLA/PCL (50/50, w/w) films were prepared by casting from 2% (w/v) dioxane solution. The solvent was allowed to evaporate at room temperature overnight. Both coalesced and solution-cast polymer films were then further dried in vacuo at 50 °C for 24 h.

b. DSC Measurements. To obtain melting temperature and heats of fusion, differential scanning calorimetry was carried out on 3−10 mg samples with a Perkin-Elmer DSC-7 thermal analyzer equipped with a cooler system. A heating rate of 10 °C/min was employed, and an indium standard was used for calibration. For evaluation of miscibility, the blends were first annealed at 200 °C for 3 min to erase previous thermal history, followed by cooling to −70 °C at 500 °C/min. For evaluating the crystallizability of PLLA and PCL, the samples were first annealed at 180 and 70 °C, respectively, for 3 min followed by quick cooling to −70 °C at 500 °C/min.

c. FTIR Spectroscopy. FTIR spectra were recorded on powdered samples pressed into KBr pellets on a Nicolet 510P FTIR spectrometer in the range between 4000 and 400 cm^{-1} with a resolution of 2 cm^{-1}.

d. Polarizing Optical Microscopy. The shape of PCL and PLLA spherulites in the films was observed with the aid of a Zeiss polarizing microscope equipped with a hot stage.

Results and Discussion. PCL−α-CD IC, PLLA−α-CD IC, and PLLA/PCL−α-CD IC were characterized by DSC, FTIR, and wide-angle X-ray diffraction. Absence of endothermic peaks corresponding to the melting points of PCL (60 °C) and PLLA (164 °C) from all IC thermograms indicates that the IC samples do not contain any free polymers. FTIR observations can demonstrate the presence of both components in the IC samples. By comparing X-ray diffraction patterns of all the above-mentioned IC samples with the patterns of valeric acid−α-CD IC and propionic acid−α-CD IC, whose crystal structures are already known as channel and cage type,[12,13] respectively, we may say that our ICs have a channel type structure.

In Figure 1 the FTIR spectra recorded for solution-cast and coalesced PLLA/PCL blends are compared. The similarity of these two spectra indicates that the coalesced PLLA/PCL blend contains both polymer components. All our attempts to dissolve the coalesced PLLA/PCL blend failed. Therefore, we could not use solution ^{13}C NMR spectroscopy to determine the ratio of the polymers in the coalesced PLLA/PCL blend.

* To whom correspondence should be addressed.

[†] Permanent address: "Gh. Asachi" Technical University, Faculty of Industrial Chemistry, Department of General Chemistry, 71 A. D. Mangeron Ave., Iasi-6600, Romania.

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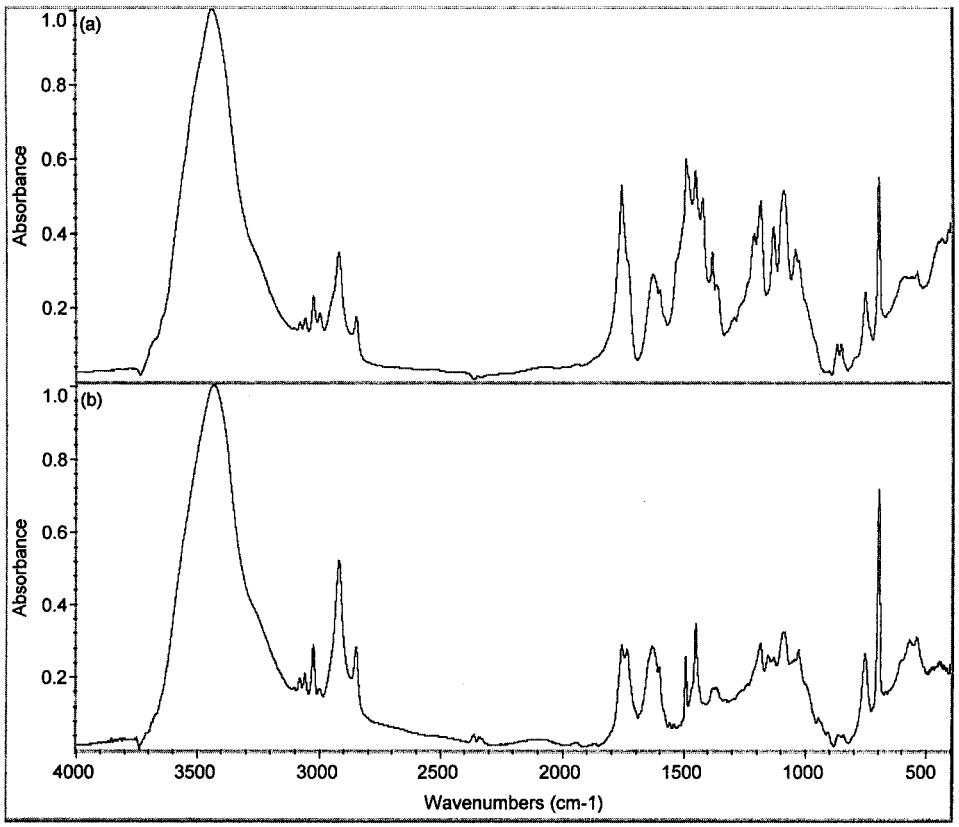

Figure 1. Fourier transform infrared spectra of (a) solution-cast and (b) coalesced PLLA/PCL blends.

Table 1. Calorimetric Data of PLLA, PCL, and PLLA/PCL Blend

	T_g (°C)			T_m (°C)		ΔH_m (J/g)		crystallinity (%)		
polymer(s)	PCL	PLLA	T_{cc} (°C)	PCL	PLLA	PCL	PLLA	PCL	PLLA	ΔH_{cc} (J/g)
pure PLLA annealed at 180 °C for 3 min		54.1	92		163.7		52.6		56.6	−41
pure PCL annealed at 70 °C for 3 min	−40.6			60.2		66.3		47.5		
PLLA coalesced from its α-CD IC annealed at 180 °C for 3 min		61.5	88.7		169.4		63.0		67.7	−22.4
PCL coalesced from its α-CD IC annealed at 70 °C for 3 min	−41.1			58.3		2.96		2.1		
PLLA/PCL blend cast from dioxane (50/50, w/w) annealed at 200 °C for 3 min			86.8	58.6	168.6	64	41	45.8	44	−20
PLLA/PCL blend coalesced from its α-CD IC (45/55, w/w) annealed at 200 °C for 3 min					166.1		5.11		5.5	

However, an estimate can be obtained by simply taking the area ratio of PLLA carbonyl (1759 cm^{-1}) and PCL carbonyl (1736 cm^{-1}) vibrational bands in the FTIR spectrum of the coalesced blend. The areas of these bands can be estimated by a deconvolution procedure. A molar ratio of 1.31:1 (PLLA/PCL; i.e., 45/55, w/w) is obtained. The efficacy of this method was confirmed by obtaining a PLLA/PCL molar ratio of 1.53:1 (i.e., 50/50, w/w) for the solution-cast blend.

The enthalpies and temperatures of fusion and crystallization of PLLA and PCL as well as their blends cast from dioxane and coalesced from α-CD IC are summarized in Table 1. On the basis of the reported enthalpies of melting for 100% crystalline PLLA and PCL, which are 93[14] and 139 J/g,[15] respectively, the crystallinity of each sample was calculated. The melting temperature of PLLA extracted from its α-CD IC is 6 °C higher than the melting temperature of pure PLLA, pointing to an enhanced stability of the coalesced PLLA chain crystals. In earlier studies, similar behavior was observed when polybutadiene was extracted from its perhydrotriphenylene clathrate[16] or for poly(ϵ-caprolactone) released from PCL−urea IC channels.[17] This may imply that extended crystals without chain folding are produced during the extraction. In contrast, PCL chains released from its α-CD IC do not exhibit the same behavior, and only a very small crystallinity was observed for the coalesced PCL sample. As we can see from Table 1, the DSC thermogram of the coalesced PLLA/PCL blend shows just one small endothermic peak corresponding to the PLLA melting point. Lack of PCL crystallinity indicates that this phase is not allowed to crystallize, and the reduction in PLLA crystallinity may be associated with its miscibility with amorphous PCL chains. An interesting feature of the coalesced PLLA/PCL blend was noted when we attempted to establish the initial crystallinity of both polymer com-

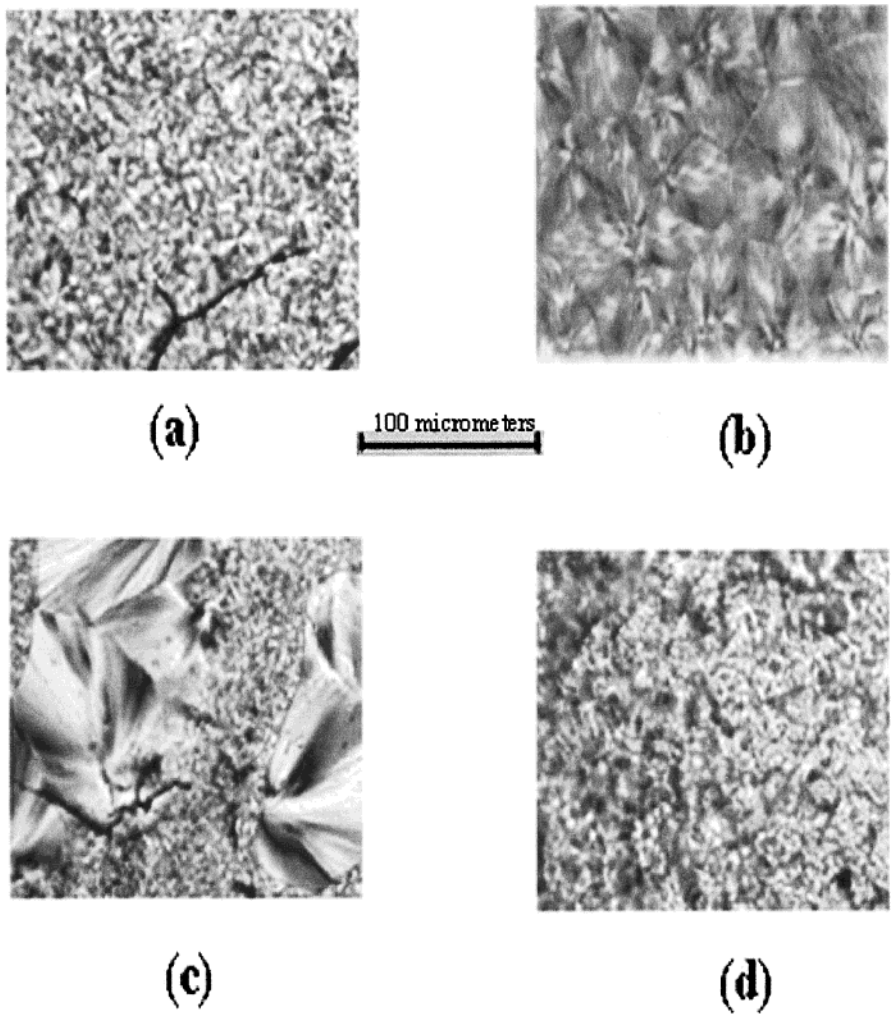

Figure 2. Polarizing photomicrographs of (a) PLLA, (b) PCL, (c) solution-cast, and (d) coalesced PLLA/PCL blends.

ponents by annealing at 200 °C for different times (1, 3, 5, or 12 h). The DSC thermograms of all the annealed blends did not undergo any alteration from the first DSC run. It appears that the PLLA/PCL blend coalesced from its α-CD IC crystals remains an intimate mixture and does not phase separate upon high-temperature annealing above the T_m of both constituent polymers. On the other hand, the DSC thermogram of the solution-cast PLLA/PCL blend exhibits two endothermic peaks centered at 58.6 and 168.6 °C, corresponding to PCL and PLLA melting points, both before and after annealing at 200 °C for 3 min.

Since the glass transition temperature of PLLA cannot be identified directly from the thermogram, we were not able to use the T_g criteria in order to judge the miscibility between PLLA and PCL. Nevertheless, the depression of the cold crystallization exotherm of PLLA observed for the solution-cast blend may indicate that the crystallization rate of PLLA can be promoted with the addition of PCL. However, according to the literature,[9] the crystallization rate of PLLA does not increase monotonically with increasing PCL composition. The bulk crystallization rate of PLLA was promoted most effectively upon blending with 10% of PCL and was not further altered by increasing the PCL composition.

Figure 2 shows the polarizing optical photomicrographs of PLLA (a), PCL (b), and their blends cast from dioxane (c) as well as coalesced from their α-CD IC (d). It is apparent that the phase-separated morphology was formed, indicating that PLLA and PCL were not fully miscible in the solution-cast blend. The spherulites with a maximum radius of 100 μm are attributed to PCL, whereas the smaller spherulites with a radius of about 20 μm are attributed to PLLA. On the contrary, the morphology observed for the coalesced PLLA/PCL blend strongly suggests that a homogeneous phase was formed. Since, based on DSC measurements, the PCL component was found only in the amorphous state, the very small well-defined spherulites in this blend can be attributed to PLLA crystals. The lack of dark regions[18] of amorphous PCL leads to the suggestion that most probably PCL molecules have been trapped in the PLLA spherulites. Further studies concerning polymer−polymer miscibility and interactions in these blends by solid-state WIM/WISE NMR spectroscopy[19] are now in progress.

In summary, it can be concluded that polymer/polymer inclusion compounds may represent an unique means to achieve intimately compatible polymer blends from normally immiscible polymers. We are currently attempting to evaluate the generality and efficiency of this approach by obtaining a compatible polymer blend starting from two normally immiscible amorphous polymers, which are coalesced from their common CD IC crystals.

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