

Poly(*para*-dioxanone)/Poly(D,L-lactide) Blends Compatibilized with Poly(D,L-lactide-*co-para*-dioxanone)

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ABSTRACT: The effect of poly(D,L-lactide-*co-para*-dioxanone) (PLADO) as the compatibilizer on the properties of the blend of poly(*para*-dioxanone) (PPDO) and poly(D,L-lactide) (PDLLA) has been investigated. The 80/20 PPDO/PDLLA blends containing from 1% to 10% of random copolymer PLADO were prepared by solution coprecipitation. The PLADO component played a very important role in determining morphology, thermal, mechanical, and hydrophilic properties of the blends. Addition of PLADO into the blends could enhance the compatibility between dispersed PDLLA phase and PPDO matrix; the boundary between the two phases became unclear and even the smallest holes were not detected. On the other hand, the position of the T_g was composition dependent; when 5%

PLADO was added into blend, the T_g distance between PPDO and PDLLA was shortened. The blends with various contents of compatibilizer had better mechanical properties compared with simple PPDO/PDLLA binary polymer blend, and such characteristics further improved as adding 5% random copolymers. The maximum observed tensile strength was 29.05 MPa for the compatibilized PPDO/PDLLA blend with 5% PLADO, whereas tensile strength of the uncompatibilized PPDO/PDLLA blend was 14.03 MPa, which was the lowest tensile strength. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 120: 544–551, 2011

Key words: poly(D,L-lactide-*co-para*-dioxanone); random copolymer; blends; compatibilization

INTRODUCTION

In recent years, blending of poly(*para*-dioxanone) (PPDO) with other biodegradable polymers has been applied not only for practical applications of new material, but also for ecological concerns.^{1–5} However, the compatibility of binary PPDO polymer blends is not fine. In our earlier work, we have investigated the blend system of PPDO with more hydrophobic poly(D,L-lactide) (PDLLA), and it is also seen that this blend system is immiscible.⁶ As we know, the compatibility of components in blends usually plays an important role in determination of the properties of the polymer blends.^{7–9} Usually, the conventional method for compatibilizing two incompatible polymers is by introducing a third component as a compatibilizer, and the addition of a random copolymer has been considered to be an effective approach.^{10,11} In the case of a random copolymer, a single polymer chain may make multiple crossings at the interface. Hence, the number of times one chain crosses the interface can be large, and the copolymer may effectively “stitch” the two

immiscible homopolymers together.¹² It is possible to enhance the compatibility between dispersed PDLLA particles and PPDO matrix by adding poly(D,L-lactide-*co-para*-dioxanone) (PLADO) into the PPDO/PDLLA blends. To our knowledge, the PPDO/PDLLA blends containing a compatibilizer have not been reported in the literature.

In this work, the effect of random copolymer (PLADO) as a potential compatibilizer for PPDO/PDLLA blends was investigated. The thermal properties of the blends were obtained using differential scanning calorimetry (DSC). Scanning electron microscopy (SEM) was used to examine the phase morphology. Polarized optical microscopy (POM) was used to characterize the spherulitic morphology, and the mechanical properties of the blends were determined from tensile test data. X-ray diffraction (XRD) was used to characterize the crystal structure, and the water contact angle was also carried out to measure hydrolysis resistance.

MATERIALS AND METHODS

Materials

PPDO and PDLLA polymers used in this study were synthesized by ring-opening polymerization of *para*-dioxanone (PDO) and D,L-lactide (LA) as described in our previous articles.^{13,14} The *para*-dioxanone was synthesized in our laboratory, dried over

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calcium hydride, and distilled under reduced pressure. The D,L-lactide was from Sichuan Dikang Sci & Tech Pharmaceutical Co., Ltd., (Chengdu, China), and was used as received. The intrinsic viscosity $[\eta]$ of PPDO and PDLLA were 1.8 and 7.0 dL/g, respectively. The viscosity-average molecular weight (M_v) of PPDO and PDLLA were 73,500 and 700,000 g/mol, respectively, and were calculated from the intrinsic viscosity $[\eta]$ using the following equations reported for PDLLA by Schindler and Harper¹⁵ and for PPDO by Sabino et al.¹⁶

$$[\eta] = KM_v^\alpha \text{ where } \alpha = 0.77 \text{ and } K = 2.21 \times 10^{-4} \text{ cm}^3/\text{g} \quad (1)$$

(PDLLA in chloroform at 25°C) and

$$[\eta] = KM_v^\alpha \text{ where } \alpha = 0.63 \text{ and } K = 79 \times 10^{-3} \text{ cm}^3/\text{g} \quad (2)$$

(PPDO in phenol/1,1,2,2-tetrachloroethane (2 : 3 v/v) at 25°C).

Amorphous PLADO used as compatibilizer for the PPDO/PDLLA blends was synthesized and characterized as described in our previous article.¹⁷ The composition of PLADO used in this work was D,L-LA/PDO = 50/50. The average number of sequential comonomer units of D,L-LA and PDO unit per PLADO chain were 4.0 and 1.0, respectively, which were determined from the 300-MHz ¹H-NMR (Bruker AM-300; Bruker Biospin, Bremen, Germany) spectrum of PLADO. The average molecular weights of the random copolymer measured with gel-permeation chromatography (Waters 1515-Styrigel HT4 and 5-2414; Waters Corp., Milford, MA) were $M_n = 78,268$ and $M_w = 165,477$.

Preparation of blends

The composition of all the blends was fixed at 80/20 (PPDO/PDLLA) by weight. The PPDO/PDLLA blends with different compatibilizer contents were prepared by solution coprecipitation, which were dissolved in 1,1,1,3,3,3-hexafluoro-2-propanol to form 10% wt/vol solutions. The solution was stirred for 6 hr, and, then, these blends were precipitated by the addition of excess ethyl alcohol. The resulting blends were dried under vacuum at 30°C for 72 hr to remove the remnant ethyl alcohol and reach the phase-equilibrium before the physical measurements. All solvents of analytical reagent grade were purchased from Kelong Chemical Factory (Chengdu, China) and used without further purification.

The blend bars with the dimension of 50 × 5 × 0.3 mm were processed by compression molding using the platen vulcanizing press (Model XLB;

Shanghai Light Industry Machinery Co., Ltd., Shanghai, China) at the processing temperature of 140°C and the processing pressure of 5.5 MPa for 5 min.

Differential scanning calorimetry

DSC was performed with a TA DSC (Model Q20; TA Instrument-Waters LLC, New Castle, DE). The blends were carefully put into the aluminum pans, heated to 140°C for 5 min to erase all thermal history, cooled to −30°C at a cooling rate of 10°C/min, and then were heated to 140°C at the same rate.

Polarized optical microscopy

Crystallinity and spherulitic morphology of the PPDO domains in the blends were studied using a POM equipped with a hot stage (Model XPN-203; Shanghai Changfang Optical Instrument Co., Ltd., Shanghai, China). Isothermal crystallization behavior was studied by heating to 150°C for 5 min and then cooling to the desired crystallization temperature (T_c), at which the PPDO was allowed to crystallize isothermally.

Scanning electron microscopy

The morphology of fracture surface of blends was examined by a scanning electron microscope (Model JSM-5900LV; JEOL Co., Tokyo, Japan) after the samples were coated with a thin layer of gold by vacuum deposition.

Tensile testing

The blend bars with dimensions of 50 × 5 × 0.3 mm were subjected to tensile testing at a drawing speed of 10 mm/min at 25°C using a SANS tensile tester (Model CMT 4503; MTS Systems Co., Ltd., Shenzhen, China). Reported values are the mean of three replicate samples. The standard used for tensile testing is ASTM D882-2009 (Standard Test Method for Tensile Properties of Thin Plastic Sheeting).

Dynamic contact angle

The advancing and receding contact angles of five replicate samples of each PPDO/PDLLA blend with various contents of PLADO were measured on the air surface of the samples using a Contact Angle System (Model DSA10; KRÜSS Instruments, Hamburg, Germany) at 20°C ± 0.5°C. Before the measurements, the samples were immersed in distilled water at 23°C for 72 hr.

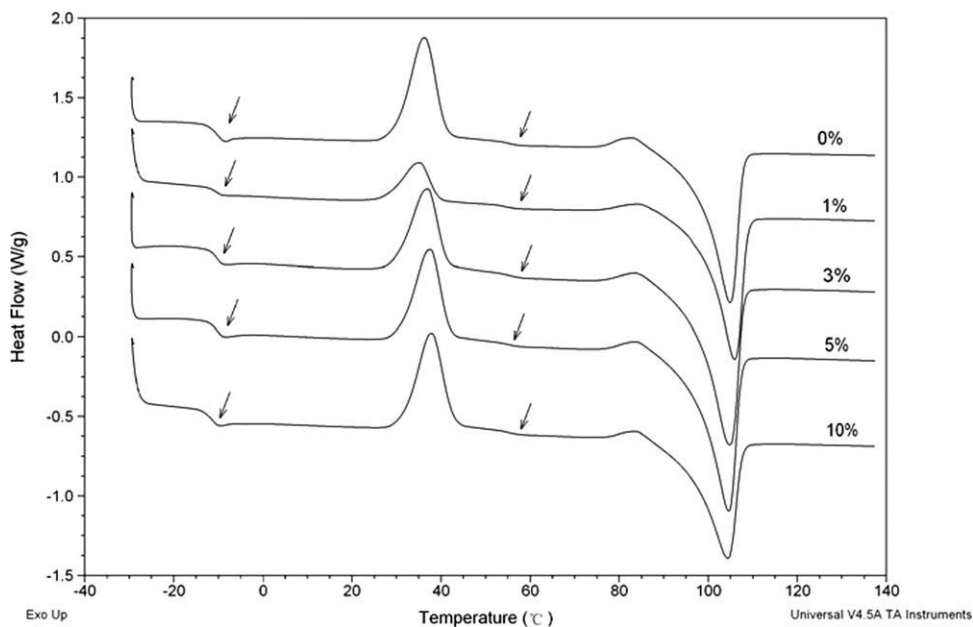


Figure 1 DSC heating curves of the PPDO/PDLLA blends with various amounts of PLADO.

X-ray diffraction

The blends were studied by XRD using a Philips X-ray diffractometer (Model X'Pert Pro; Koninklijke Philips Electronics N.V., Amsterdam, the Netherlands) equipped with a Ni-filtered Cu K α ($\lambda = 0.1542$ nm) radiation source operated at 40 kV and 30 mA. Samples were scanned from 10° to 40° (2 θ).

RESULTS AND DISCUSSION

Thermal analysis

The glass-transition temperature (T_g), the crystallinity enthalpy (ΔH_c), and the melting temperature (T_m) of blends were determined from the DSC curves in Figures 1 and 2. The relative degree of crystallinity is calculated from the equation

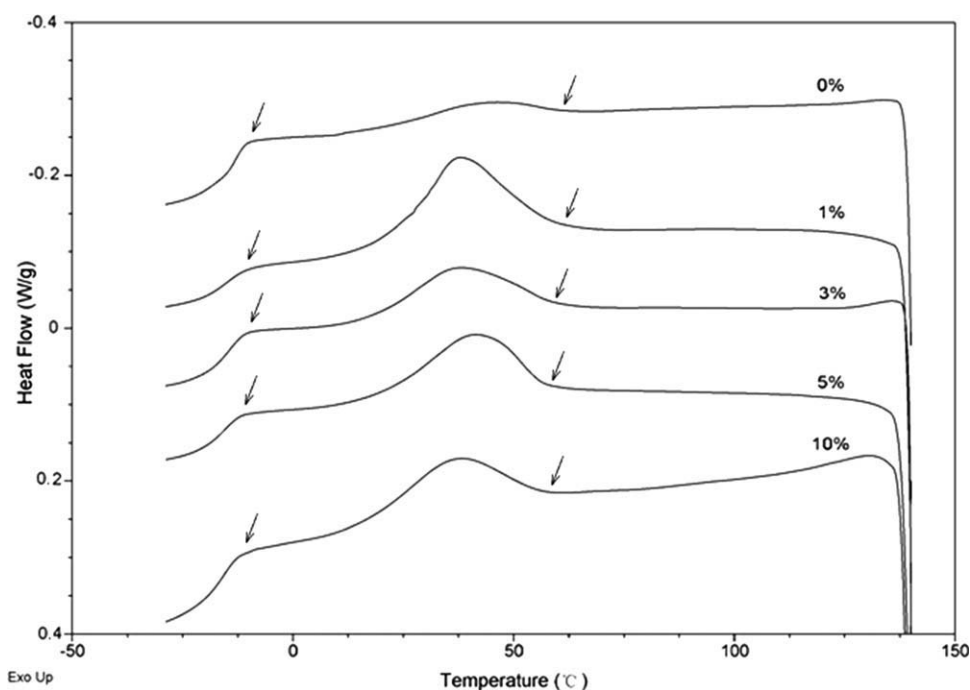


Figure 2 DSC cooling curves of the PPDO/PDLLA blends with various amounts of PLADO.

TABLE I
Thermal Properties of PPDO/PDLLA Blends with Various Contents of PLADO

PLADO content (%)	T_g^{PPDO} (°C)	T_g^{PDLLA} (°C)	$\Delta H_c^{\text{cooling}}$ (J/g)	$\Delta H_c^{\text{heating}}$ (J/g)	X_t (%)	T_m^{PPDO} (°C)
0	-10.02	54.91	3.69	26.14	12.36	104.91
1	-10.39	54.13	15.91	10.06	61.26	105.92
3	-10.41	55.66	10.80	21.85	33.08	104.83
5	-9.88	53.35	13.84	19.74	41.21	106.73
10	-10.12	56.18	8.90	27.61	24.38	106.40

$X_t = \Delta H_c^{\text{cooling}} / \Delta H_c^{\text{total}}$, where $\Delta H_c^{\text{cooling}}$ is the crystallization enthalpy in the cooling scan and $\Delta H_c^{\text{total}}$ is the sum of crystallization enthalpy in the cooling scan and in the heating scan.¹

DSC is a well-known method for studying the miscibility of polymer blends, based on the appearance of a single T_g between those of the homopolymers. The arrows indicate two independent glass transitions for PPDO/PDLLA blends; the left is T_g of PPDO and the right is T_g of PDLLA as shown in Figure 1. However, there were some changes in the T_g 's of PPDO and PDLLA with variation in PLADO content in the blends. It was found that the addition of compatibilizer into the PPDO/PDLLA blends slightly reduced the T_g of PDLLA and elevated T_g of PPDO, respectively, because the compatibilizer PLADO could effectively enhance interfacial adhesion strength. This indicated that the compatibilized PPDO/PDLLA blend with 5% PLADO had better homogeneity.¹⁸ However, when more compatibilizer was added, the compatibility did not continue improving, and the T_g distance between PPDO and PDLLA became longer again. It was because the micelles were formed beyond the critical micelle concentration that was required to saturate the interface between two immiscible polymers, and further addition of more compatibilizers would not improve the interfacial properties.¹⁹ A similar conclusion was drawn for poly(L-lactide)/poly(ethylene-octene),²⁰ ethylene-propylene-diene rubber/poly(trimethylene terephthalate),²¹ polystyrene (PS)/acrylonitrile-butadiene rubber,²² and PS/polybutadiene.²³

Table I lists the thermal properties data of all different blends as determined from the DSC curves. The $\Delta H_c^{\text{cooling}}$ of blends was also dependent on the blend composition; the compatibilized PPDO/PDLLA blends presented an improvement in the $\Delta H_c^{\text{cooling}}$, and the crystallinity enthalpy in cooling scans of the compatibilized PPDO/PDLLA blends with 1, 3, 5, and 10% PLADO reached 15.91, 10.8, 13.84, and 11.52 J/g, which were 4.31, 2.93, 3.75, and 3.12 times of simple binary polymer blend (3.69 J/g), respectively. An increase in the $\Delta H_c^{\text{cooling}}$ was usually related to an increase in the relative degree of crystallinity,^{1,24} and the relative degree of crystallinity of the PPDO simultaneously increased from 12.36% to

61.26, 33.08, 41.21, and 24.38% for the PPDO/PDLLA blends with 1, 3, 5, and 10% compatibilizer, respectively. It was believed that PLADO as nucleating agent induced the earlier formation of PPDO nuclei and also improved the crystallinity of PPDO. Sabinio⁴ reported similar result for PPDO/PCL blends.

The peak temperature of endotherm for the PPDO phase in the PPDO/PDLLA blends with 1, 3, 5, and 10% PLADO was 105.92, 104.83, 106.73, and 106.4°C, respectively, and did not change significantly. These temperatures are similar to that of the corresponding uncompatibilized blend, located at 104.91°C. This phenomenon could also be found in our previous work.⁸

Morphologies

Fracture surfaces were obtained by fracturing molded bars of the 80/20 PPDO/PDLLA blends with various contents of compatibilizer in liquid N₂. The microstructure was examined using SEM (Fig. 3) ($\times 5000$), revealing a sea-island structure on blends; the dispersed PDLLA phase formed spherical particles distributed inside the PPDO matrix, and the average dimension of spherical particles was smaller than 5 μm in the PPDO/PDLLA blends. However, there were some differences in their morphologies. As shown in Figure 3(a), the interface between PPDO and PDLLA was poor, the phase separation between PPDO and PDLLA could be clearly observed, the boundary between dispersed phase and PPDO matrix was distinct, and the small holes with various diameters could also be detected, which is expected because hydrophilic PPDO and hydrophobic PDLLA are thermodynamically immiscible. The addition of 1% or 3% compatibilizer to the PPDO/PDLLA blend did not show clear changes in the interface [Fig. 3(b,c)].²⁵ On the contrary, the morphology of the phase interface was improved significantly by the addition of 5% PLADO because the small holes disappeared and interface became unclear [Fig. 3(d)], which was ascribed to the reduction in interfacial tension between dispersed phase and PPDO matrix and the improvement of compatibility and interfacial adhesion. It was more evident that blend with 5% PLADO presented some

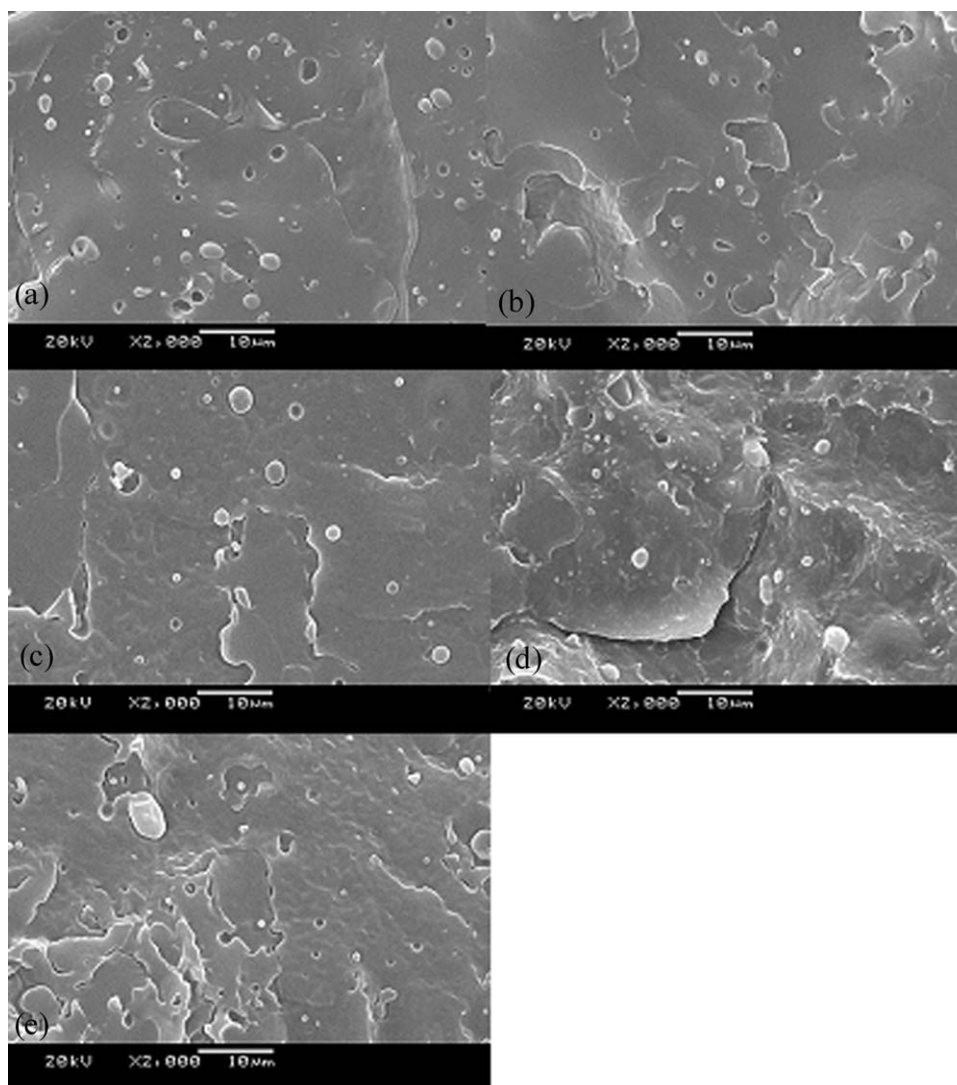


Figure 3 Scanning electron micrographs of the fracture surfaces of PPDO/PDLLA blends with various amounts of PLADO: (a) 0%; (b) 1%; (c) 3%; (d) 5%; and (e) 10%.

compatibility. Braun et al.²⁶ also observed that phase interface became unclear for the PS/polyvinyl chloride blends with a certain amount of copolymer.

However, the addition of 10% copolymer made phase interface smooth and distinct again as shown in Figure 3(e). According to the previous study of Brown et al.,²⁷ the excess compatibilizer tends to form the micelles in the PS/PMMA blends, and the micelles were located in the PMMA phase because the MMA segment in the copolymer was rich. Because the copolymer PLADO used in this study was rich in the D,L-LA segments, which means that the D,L-LA content in the copolymer PLADO is higher, the excess PLADO in the PPDO/PDLLA blends seemed to form micelles; as the micelle formation starts, some of the copolymer compatibilizer at the interface had already left the interface, leading boundary between dispersed phase and PPDO matrix obviously.²⁸ Thus, the content of compatibilizer

might dominate the morphological variations of the phase interface.²⁹

Spherulitic morphology

Figure 4 shows a series of polarized optical micrographs of PPDO spherulites isothermally crystallized at 60°C ($\times 500$), indicating that PPDO was able to crystallize with a spherulitic morphology even in the presence of 10% PLADO. However, the spherulitic morphology of PPDO changed with the addition of the amorphous PLADO component. The PPDO/PDLLA blend with 1% and 3% PLADO [Fig. 4(b,c)] showed well-defined spherulites with apparently regular concentric rings and Maltese cross extinction patterns, a crystal behavior similar to simple binary polymer blend in Figure 4(a). The spherulites still exhibited the Maltese cross extinction pattern, but the concentric rings were now difficult to observe

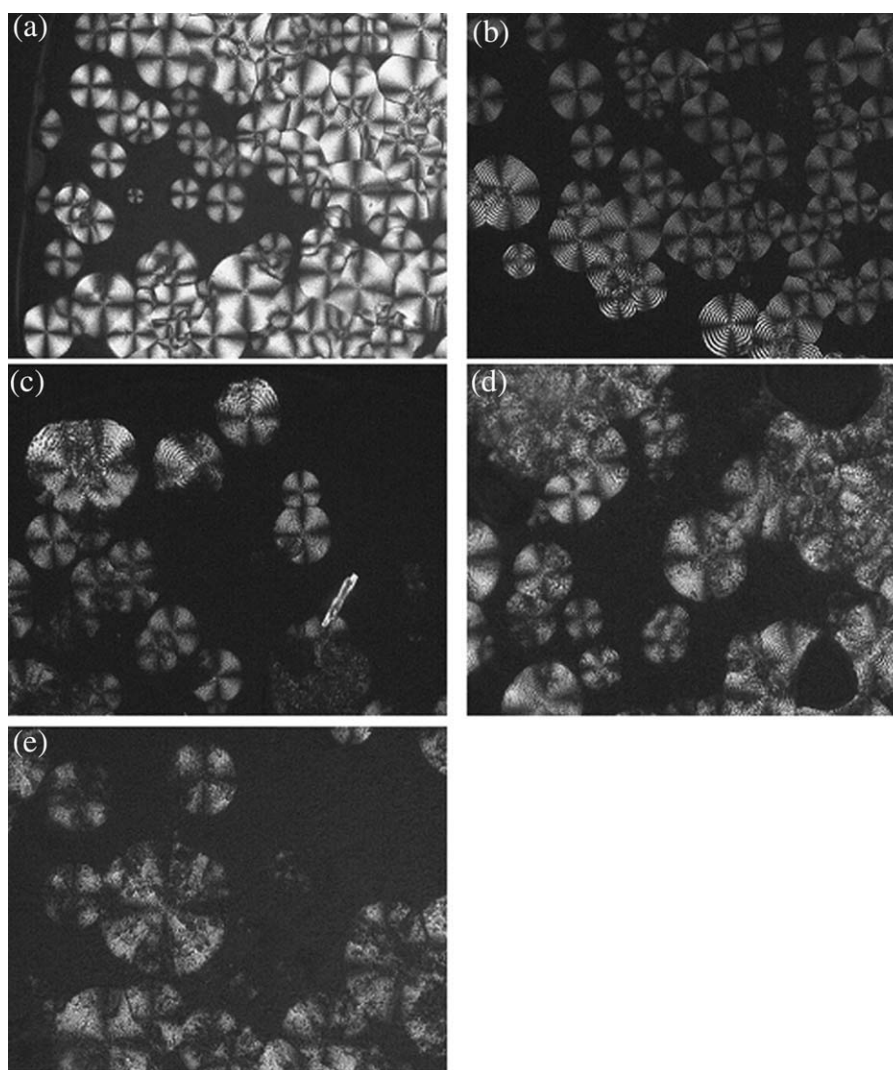


Figure 4 POM photos of PPDO/PDLLA blends with various amounts of PLADO isothermally crystallized at 60°C: (a) 0%; (b) 1%; (c) 3%; (d) 5%; and (e) 10%.

for the blend with 5% PLADO [Fig. 4(d)]. When the PLADO component reached 10%, the spherulites became coarser as can be seen in Figure 4(e) where the concentric rings were totally disrupted, suggesting that the crystalline phase of blends with higher PLADO component had less regularity. POM observation of the isothermal crystallinity of PPDO in the blends led to a conclusion: the various contents of PLADO would influence the spherulitic morphology of PPDO in PPDO/PDLLA system.³⁰

Mechanical properties

Mechanical properties of both the uncompatibilized and compatibilized PPDO/PDLLA blends were evaluated by tensile strength and elongation-at-break measurements. Table II presents the mechanical properties of the PPDO/PDLLA blends with various contents of compatibilizer. The addition of PLADO led to a large increase in tensile strength of blends.^{31,32} The

tensile strength of the compatibilized PPDO/PDLLA blends with 1, 3, 5, and 10 PLADO increased by 58.95, 66.64, 107.06, and 73.06%, respectively. The values of tensile strength of the compatibilized blends were higher than that of the uncompatibilized blend, and it was found that the tensile strength increased with the addition of PLADO up to 5% and decreased slightly above 5%. Consequently, a maximum tensile strength

TABLE II
Mechanical Properties of PPDO/PDLLA Blends with Various Contents of PLADO

PLADO content (%)	Tensile strength (MPa)	Elongation at break (%)
0	14.03 ± 4.80	79.50 ± 4.78
1	22.30 ± 0.90	20.97 ± 7.09
3	22.38 ± 0.67	33.59 ± 6.27
5	29.05 ± 4.10	41.39 ± 5.06
10	24.28 ± 1.76	30.26 ± 9.48

TABLE III
**Advancing and Receding Contact Angles of PPDO/
 PDLLA Blends with Various Contents of PLADO**

PLADO content (%)	Advancing (°)	Receding (°)
0	51.4 ± 1.2	41.0 ± 0.6
1	53.2 ± 0.9	44.9 ± 0.5
3	55.6 ± 1.1	46.8 ± 1.8
5	58.2 ± 0.4	48.0 ± 0.9
10	60.8 ± 1.9	53.4 ± 1.0

of 29.05 MPa was exhibited by the PPDO/PDLLA blend with 5% PLADO, whereas the uncompatibilized blend exhibited the lowest tensile strength of 14.03 MPa. This result indicated that the weak interfacial adhesion associated with the incompatibility of simple binary polymer blend. At the same time, it was supposed that the mechanical properties of the blends were influenced strongly by the contents of the compatibilizer PLADO.³³

A significant variation in elongation at break was also observed in the compatibilized blends. This variation was dependent on the contents of PLADO in the blends; the addition of PLADO reduced the elongation at break of the PPDO/PDLLA blends. The maximum elongation at break of 79.50% was exhibited by simple binary polymer blend, whereas the addition of 1% PLADO reduced the elongation at break to 20.97%. It was likely that an increase in relative degree of crystallinity of the material leads to a decrease in the elongation at break of blends.³⁴ However, the compatibilized PPDO/PDLLA blend with 5% PLADO showed the highest elongation at break (41.39%) in all compatibilized blends. It was obvious that a certain amount of PLADO could eliminate the phase interface and give fine dispersion of PDLLA domains in the PPDO matrix. Overall mechanical properties of the compatibilized blends were somewhat improved, especially in the tensile strength. These behaviors might be connected with the improvement in compatibility observed by SEM and DSC,^{3,35} resulting in an increase in the mechanical properties.

Water contact angle

The surface water wettability of PPDO/PDLLA blends was assessed using dynamic contact angle analysis because this parameter is important for hydrolytic degradation behaviors of blends. As we know, polymer blends with more hydrophobic content exhibited a much smaller degradation rate when subjected to hydrolytic degradation *in vivo*, which means the breakdown of a material in the presence of water. The advancing and receding angles of all blends examined in this study are presented in Table III. The resultant advancing and

receding contact angles were observed to statistically increase with the addition of the amorphous PLADO component. In all cases, the presence of PLADO led to a significant improvement in material hydrophobicity. It was because that the D,L-LA segments of PLADO used in this study were rich; it means that D,L-LA content in the copolymer PLADO is higher, which made PLADO to show hydrophobicity.³⁶ The effects of D,L-LA segments on the surface properties might be attributed to the presence of a methyl side-chain in the polymer backbone. The hydrophobic nature of PLADO made the compatibilized blend bars less hydrophilic than the uncompatibilized blend samples.

XRD analysis

Figure 5 shows X-ray powder diffraction pattern of PPDO/PDLLA blends with various contents of compatibilizer. The major PPDO peak at around $2\theta = 22^\circ, 24^\circ,$ and 29° ^{37,38} could be detected in all blends. The peak shape of PPDO in XRD patterns remained constant because the interlayer distance of PPDO was basically unchanged ($d = 4.0, 3.7,$ and 3.0 nm). However, the peak corresponding to PDLLA and PLADO were not detected because both polymers were amorphous. This result showed that PLADO content in this system did not influence the crystal-line structure of PPDO.

CONCLUSIONS

Owing to the poor interfacial adhesion and bigger particle size of the dispersed phase, PPDO/PDLLA binary blends have poor mechanical properties. In this work, the possibility of compatibilizing 80/20 PPDO/PDLLA blends using PLADO was explored.

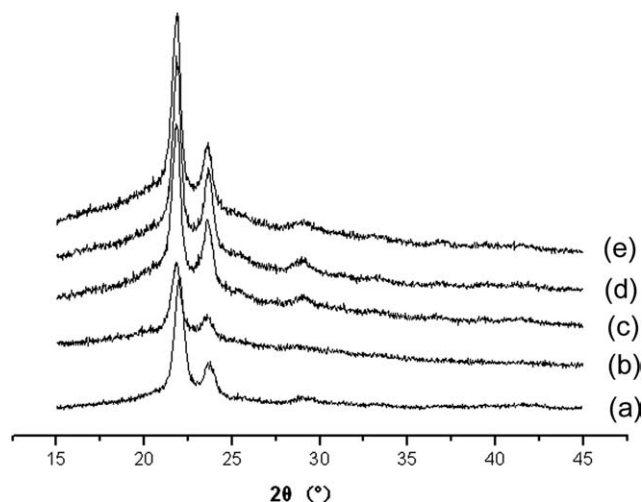


Figure 5 X-ray diffractograms of the PPDO/PDLLA blends with various amounts of PLADO: (a) 0%; (b) 1%; (c) 3%; (d) 5%; and (e) 10%.

The influence of compatibilization on the morphology, thermal, mechanical, and hydrophilic properties of the blends has been studied. The incorporation of PLADO into the PPDO/PDLLA blends leads to a fine adhesion between the phases, where the boundary between dispersed particles (PDLLA) and continuous phase (PPDO) becomes unclear. In particular, a relation is found between homogeneity and contents of PLADO in the blend; the compatibility of the blends increased with the addition of the small amount of the compatibilizer, followed by a leveling off at higher content. When 5% PLADO was added into the blend, the T_g difference between PPDO and PDLLA was reduced, and the compatibilized PPDO/PDLLA system with 5% PLADO showed the best mechanical properties and the strongest adhesion strength compared with the uncompatibilized PPDO/PDLLA blend. These behaviors provided further evidence for the improved compatibility or the reinforced adhesion between dispersed PDLLA phase and PPDO matrix in the PLADO-compatibilized blends.

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