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Yottha Srithep , Dutchanee Pholharn; John Morris



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# Injection-Molded Poly(L-lactic acid)/Poly(D-lactic acid) Blends: Thermal and Mechanical Properties

Yottha Srithep<sup>1, a)</sup>, Dutchanee Pholharn<sup>2</sup> and John Morris<sup>1</sup>

<sup>1</sup>*Manufacturing and Materials Research Unit, Dept. of Manufacturing Engineering, Faculty of Engineering, Maharakham University, Maharakham 44150, Thailand*

<sup>2</sup>*Dept. of Chemistry, Faculty of Science and Technology, Rajabhat Maha Sarakham University, Maharakham 44000, Thailand*

<sup>a)</sup> Corresponding Author: yottha.s@msu.ac.th

**Abstract.** Poly(L-lactic acid) (PLLA)/Poly(D-lactic acid) (PLLA/PDLA) blends ranging from neat PLLA to neat PDLA were prepared by hand mixing, which removed the need for melt mixing, followed by injection molding at 200°C to produce tensile specimens. Thermal properties, crystalline structure and mechanical properties were measured by differential scanning calorimetry, thermogravimetric analysis, wide-angle X-ray diffraction and tensile testing. In blends ranging from 10% to 30% PDLA in PLLA, the PDLA melting peak was absent and was replaced by the stereocomplex melting peak at 210°C, which is about 40 degC higher than that for neat PLLA or PDLA. The reverse blending of PLLA into PDLA showed similar behavior. Surprisingly, three melting peaks (for PLLA, PDLA and the complex crystal) appeared in the 1:1 PLLA/PDLA blend because the source PLLA and PDLA initially had different degrees of crystallinity and did not mix well. However, the blends containing stereocomplex crystallites have higher thermal resistance and can be worked, without melting, at higher temperatures than the neat polymers: yet, the mechanical properties were not affected.

**Keywords:** Stereocomplex, Injection molding, Poly(lactic acid)

**PACS:** 83.50.Uv, 82.35.Pq, 87.15.rp,

## INTRODUCTION

Renewable sources and biodegradability of Poly(lactic acid) (PLA) or polylactide makes it a promising and eco-friendly polymer [1]. PLA or modified PLA is a good substitute for conventional oil based thermoplastics because of its good mechanical strength, toughness and workability [2]. PLA has two enantiomers, poly(L-lactic acid) (PLLA) and poly(D-lactic acid) (PDLA). Blending of PLLA with PDLA leads to the formation of a stereocomplex, which has a melting temperature around 230°C, 50 degC higher than homocrystallized PLLA or PDLA [3]. Solution and melt blending are commonly used for generating stereocomplex crystallites. However, the blends, in previous studies, were mostly prepared through solution blending which requires environmentally damaging, volatile organic solvents to facilitate processing [4, 5]. Moreover, melt blending needs to be processed at the elevated temperature at which the stereocomplex melts, which induces significant degradation of the homopolymer [3].

In this study, we prepared PLLA/PDLA blends by simply hand mixing and injection molding. Crystallization experiments and phase-separation behavior were evaluated by differential scanning calorimetry (DSC). Finally, we investigated the mechanical properties of the blends with tensile tests.

## EXPERIMENTS

### Materials

The materials used in this study were PLLA and PDLA. PLLA (NatureWorks® 3052D), density 1.24 g/cm<sup>3</sup>, had a high optical purity, containing mainly L-lactic acid with 1.4% ± 0.2% D-lactic acid. PDLA (D100-M) with L-isomer lower than 0.3% was purchased from Sulzer Chemtech Ltd, Winterthur, Switzerland. Table 1 summarizes the properties of the polylactides used. Molecular weights were measured with a gel permeation chromatograph (1260 Infinity II GPC, Agilent Technologies).

## Sample Preparation

Hand mixed PLLA and PDLA pellets containing 10, 30, 50, 70 and 90% of PDLA by weight were prepared. PLA is susceptible to hydrolysis during the processing, therefore prior to injection molding; the mixed pellets were dried in an oven at 80°C for 10 h to remove moisture. The mixed pellets were then injection molded at 200°C to produce tensile bars (ASTM D638) using a Charentut INJ-58T (Thailand) injection molding machine. Reference samples of pure PLLA and PDLA were prepared under the same conditions.

TABLE 1. Properties of poly(lactic acid) used

Polymer	Manufacturer's data				Our measurements			
	$T_m$ (°C)	D-unit content (%)	MFI		Crystallinity	$M_w$ (kg/mol)	Opacity	PDI
			g/10 min	Temp (°C)				
PLLA	145-160	1.4	14	210	amorphous	160	clear	1.53
PDLA	175	99.7	14-15	190	40-50%	95	opaque	1.60

## Differential Scanning Calorimetry (DSC)

Thermal properties of the blends were measured by a differential scanning calorimeter (Perkin–Elmer DSC, 4000). Specimens of 4 to 5 mg were cut from the center of the injection molded bars and placed in aluminum pans. To monitor the stereocomplex formation, samples were heated from -10 °C to 280 °C at a rate of 10degC/min. The cold crystallization temperature ( $T_{cc}$ ) and its enthalpy ( $\Delta H_{cc}$ ), homo-melting temperature ( $T_{m1}$ ) and its enthalpy ( $\Delta H_{f1}$ ), stereocomplex melting temperature and its melting enthalpy ( $T_{m2}$  and  $\Delta H_{f2}$ ) were determined.

## Wide-angle X-ray diffraction (WAXD)

Wide-angle X-ray diffraction (WAXD) patterns of injection-molded pure PLLA, pure PDLA and the blends were measured with an X-ray diffractometer (Bruker/D8 Advance BrukerBioSpin AG). WAXD samples were taken from injection molded specimens and mounted on the XRD platform for analysis. A  $2\theta$  range from 2° to 40° in reflection mode was scanned at 2°/min with a computer-controlled wide angle mode goniometer. The source was a Cu K $\alpha$  line with a thin Ni filter.

## Tensile Testing

Tensile tests on the injection molded tensile specimens followed the ASTM D638 standard. The static tensile modulus, strength and strain-at-break were measured at 25 °C and a relative humidity of 50 ± 5% on an NRI-TS501 universal testing instrument. The tensile tests were performed on all specimens using an initial load of 0.5 N and a constant crosshead speed of 10 mm/min. Five specimens of each sample group were tested and averaged.

## RESULTS AND DISCUSSION

### Thermal Properties

Figure 1 shows DSC thermograms of injection-molded PLLA blended with varying amounts of PDLA. The curves revealed (1) a glass transition temperature ( $T_g$ ) near 60 °C, (2) a cold crystallization peak between 92 and 116 °C, (3) an endothermic fusion peak for homocrystals (melting peak,  $T_m$ ) with a maximum between 150 to 170 °C and (4) an endothermic fusion peak for stereocomplex crystals (stereocomplex melting peak,  $T_{m,sc\ crystal}$ ). During injection molding, the crystallization process was partially constrained by the high cooling rate. As a result, it is typical for injection molded parts to exhibit a cold crystallization peak ( $T_{cc}$ ) during the DSC test, when the specimens are re-heated, regain some mobility and further crystals can be formed.

Table 1 shows the temperature and enthalpy from the DSC test for different PLLA/PDLA ratios. Pure PLLA exhibits a glass transition temperature ( $T_g$ ) around 58°C, cold crystallization temperature around 116°C and a melting temperature ( $T_{m1}$ ) at about 151°C. PDLA (sourced from Sulzer) is significantly different in molecular weight and degree of crystallinity and opacity – see Table 1. The higher degree of crystallinity results from

difference in the manufacturing process and leads to higher opacity compared to the amorphous PLLA. Thus the glass temperature of PDLA was around 59°C (close to PLLA at about 58°C), but the cold crystallization temperature around 92°C and  $T_{m1}$  at around 175°C are more than 20°C higher than those of pure PLLA. Moreover, the melting enthalpy of PDLA is higher than that of PLLA which indicated that PLLA was almost amorphous while PDLA was easier to crystallize. For PLLA/PDLA blends, we found an apparent melting temperature ( $T_{m2} \approx 210^\circ\text{C}$ ) of stereocomplex PLA crystallites (sc-crystallites), which shows a complex crystal  $T_m$  of 50°C higher than that of homocrystal PLLA or PDLA [3, 6]. This is a clear evidence of complex formation between PLLA and PDLA. From the DSC traces, it is apparent that the PLLA/PDLA complex crystal ( $T_m \approx 210^\circ\text{C}$ ) is present, not only in the 1:1 PLLA:PDLA mix, but also for any mixture. The addition of 10% PLLA in PDLA (PLLA/PDLA: 10/90) displays both complex and homo-PDLA crystals and no homo-PLLA. This indicates that the small quantity of PLLA was converted entirely to complex crystals. Similarly, the addition of 10% PDLA into PLLA did not show homo-PDLA. Moreover, as the initial source PDLA had a high degree of crystallinity (see Table 1), the initial crystals nucleated the formation of stereocomplex crystals and the addition of 10% - 30% PDLA into PLLA formed more stereocomplex crystals than the reverse - adding the same fractions of PLLA into PDLA. Further, when PDLA and PLLA were blended in equal amounts, the two components did not mix well and showed some apparent separation.

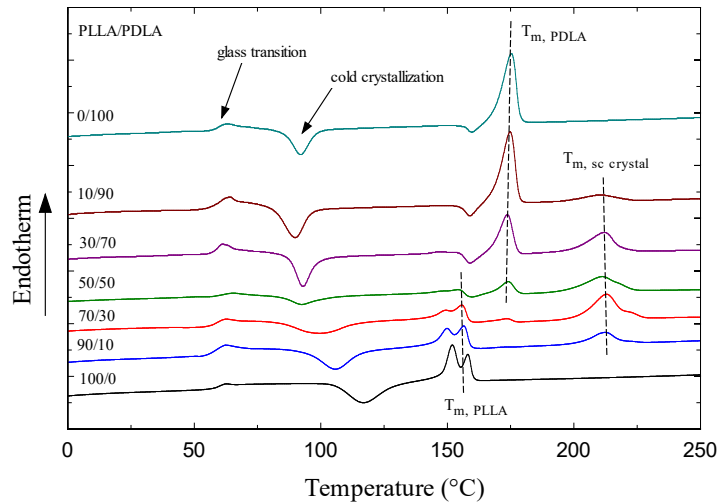


FIGURE 1. DSC thermograms of PLLA/PDLA blends

TABLE 2. DSC data for PLLA/PDLA blends

Samples PLLA/PDLA	$T_g$ (°C)	Cold crystallization		Melting 1		Melting 2	
		$T_{cc}$ (°C)	$\Delta H_{cc}$ (J/g)	$T_{m1}$ (°C)	$\Delta H_{f1}$ (J/g)	$T_{m2}$ (°C)	$\Delta H_{f2}$ (J/g)
1. 0/100	58.7	92.2	16.5	175.2	56.7	-	-
2. 10/90	57.5	89.7	22.5	174.7	62.3	210.7	1.21
3. 30/70	57.9	92.9	20.8	173.6	32.3	212.2	19.0
4. 50/50	62.3	92.4	9.5	174.0	15.6	211.2	17.4
5. 70/30	58.0	99.5	22.2	155.8	22.2	212.8	27.2
6. 90/10	59.1	105.8	23.1	156.4	26.7	212.3	8.7
7. 100/0	59.6	116.9	23.1	152.0	25.7	-	-

## Wide-Angle X-ray Diffraction

Figure 2 shows WAXD profiles of PLLA/PDLA blends of various compositions measured at room temperature (ca. 25°C). the pure PLLA specimens (100/0) appeared mostly amorphous and only one broad halo with a maximum at  $2\theta \approx 16^\circ$  was observed with no significant crystal peak(s) [7]. On the other hand, for pure homocrystal PDLA, the diffraction peaks located at  $2\theta \approx 16.2^\circ$  and  $18.6^\circ$  correspond to the  $\alpha$ -form homocrystal [8, 9]. Consistent with the DSC results, this indicated the PDLA was easier to crystallize than PLLA. In the blends, in addition to the characteristic homocrystal peaks ( $16.2^\circ$  and  $18.6^\circ$ ) which decreased, additional diffraction peaks at  $2\theta \approx 11.6^\circ$ ,  $20.6^\circ$  and  $23.5^\circ$  were assigned to planes of the PLA stereocomplex crystallites (sc) [7, 10, 11]. Also consistent with the DSC results, the homocrystal PLLA or PDLA crystallizes with sc-crystallites in the injection-molded PLLA/PDLA

blends. Further, the number of sc-crystallites for PLLA/PDLA: 70/30 was higher than that for 30/70 because, as noted in section 3.1, the source PDLA initially contained more crystals than the PLLA.

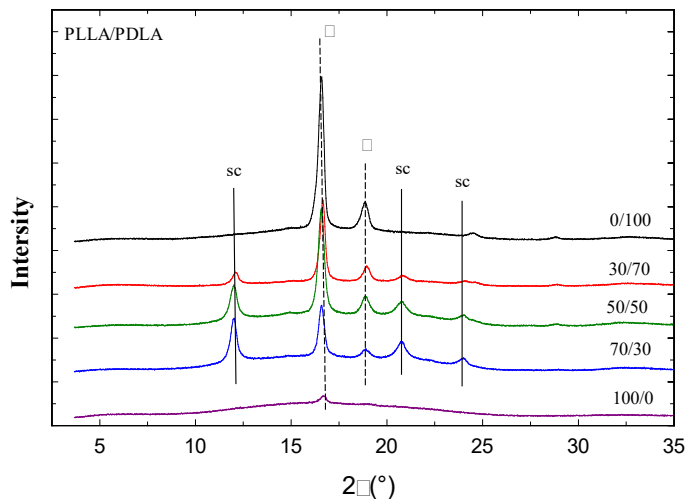


FIGURE 2. WAXD scans for PLLA/PDLA blends with various compositions

## Tensile Properties

The mechanical properties of PLLA/PDLA blends depend on their composition, processing conditions and resulting structure [12]. A few papers have reported the mechanical properties of injection-molded PLLA/PDLA blends [12]. Figure 3 show the results of tensile tests on the injection-molded components of the PLLA/PDLA, according to ASTM-D638. Strength, elongation at break and modulus were measured. Pure PLLA which has a higher molecular weight (Table 1) than pure PDLA had higher strength, modulus and strain at break than PDLA. The weight average molecular weight ( $M_w$ ) of PLLA was around 160 kg/mol while the PDLA was around 95 kg/mol. As shown in Figure 3a, pure PLLA had a maximum tensile strength around 50 MPa, whereas pure PDLA was lower at around 22 MPa. The mechanical properties of PLLA/PDLA blends cannot be improved by stereocomplex structure. Xu et.al reported similar behavior of injection-molded PLLA/PDLA blends [13]. However, the increased PLLA content in PDLA improved the tensile strength gradually. Similarly, for elongation at break and tensile modulus, higher fractions of PLLA enhanced both properties.

## CONCLUSIONS

Although, the sources of PLLA and PDLA materials clearly had some different characteristics, the results presented here focus on the presence of the stereocomplexes and only to a small extent on the different sources. In this article, PLLA/PDLA blends were prepared by simply mixing and injection molding below the melting temperature of their stereocomplexes which reduced further thermal degradation. Adding 10% to 30% PDLA into PLLA did not show the melting peaks of PDLA but formed complex crystals only and the melting point of formed stereocomplex crystallite is about 210°C compared to 150-175°C for the homocrystals. The reverse behavior (adding 10% to 30% PLLA into PDLA) was similar but from a source of lower crystallinity. The blends in which the stereocomplexes were formed showed higher melting temperatures and thus can be worked without melting at higher temperatures. However, the formed stereocomplex crystallites did not change the mechanical properties of PLLA/PDLA blends.

Further work needs to evaluate the effect of the molecular weight of the components of the PLLA/PDLA blends.

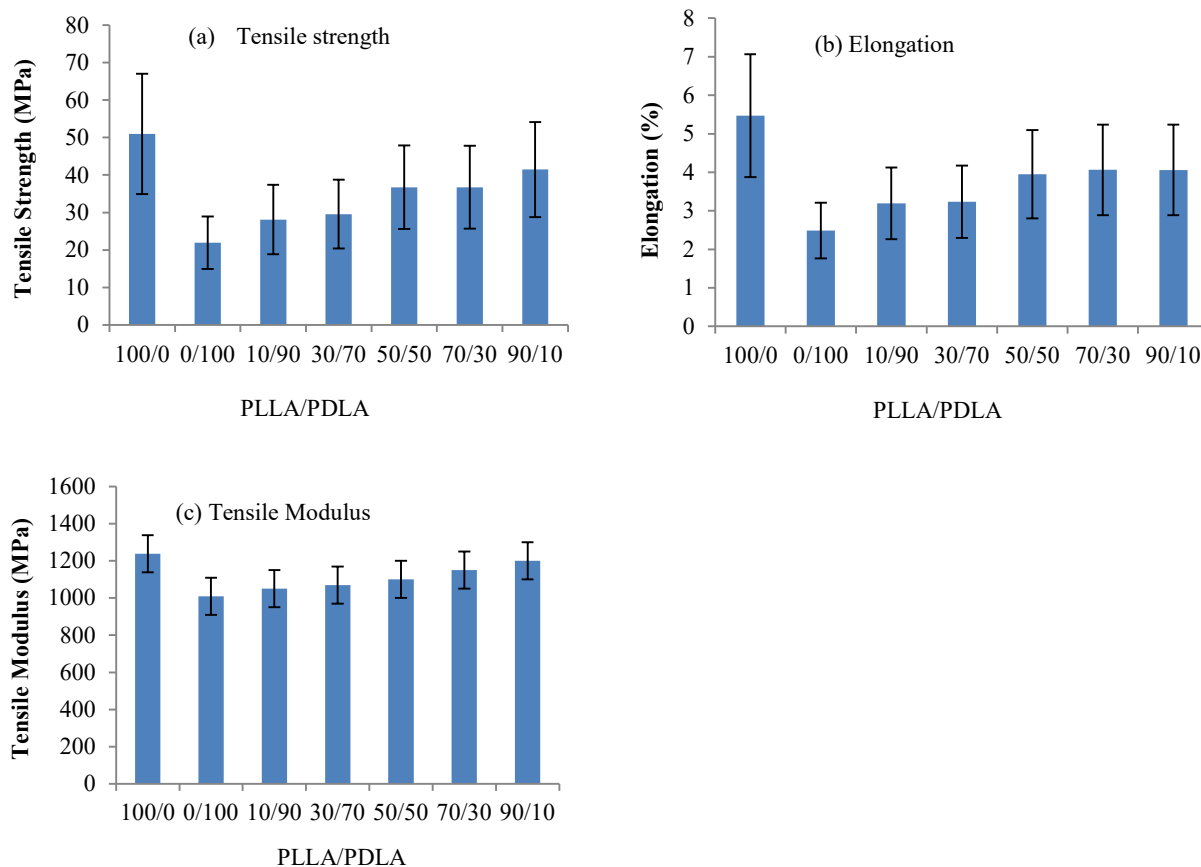


FIGURE 3. Tensile strength, elongation at break and tensile modulus of PLLA/PDLA blends

## ACKNOWLEDGEMENTS

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