Effect of molecular weight of poly(L-lactic acid) on the stereocomplex formation between enantiomeric poly(lactic acid)s blendings

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Abstract. The effect of molecular weight of poly(L-lactic acid) on the stereocomplex formation between poly(L-lactic acid) (PLLA) and poly(D-lactic acid) (PDLA) was investigated. Films of 1:1 blend were prepared from PLLA with molecular weight of 125, 180 and 209 kg/mol and PDLA with molecular weight of 150 kg/mol by a solution cast method. Thermal properties, crystalline structure and mechanical properties were measured by differential scanning calorimetry (DSC), wide-angle X-ray diffraction (XRD) and tensile testing. Blending lowest molecular weight PLLA (M_w 125 kg/mol) with PDLA showed highest stereocomplex formation with melting temperature more than 50°C compared to that of homocrystallites. As the molecular weight of PLLA became higher, the stereocomplex formation was lower. Films with higher stereocomplex formation also had higher mechanical properties.

1. Introduction
Poly(lactic acid) (PLA) is a plant-derived and compostable polymer with good mechanical, optical and barrier properties [1]. PLA has two enantiomeric isomers, poly(L-lactic acid) (PLLA) and poly(D-lactic acid) (PDLA). For improving thermal/mechanical properties and hydrolysis resistance of poly(lactic acid) (PLA)-based materials, blending PLLA and PDLA leads to the formation of a stereocomplex, which has a melting temperature around 220°C, 50°C higher than homocrystallized PLLA or PDLA [2, 3]. Characteristics of the two components; i.e., the molecular weight, optical purity and chain architecture (linear or branched) have influence over the kinetics and extent of the stereocomplex formation between PLLA and PDLA [4].

In spite of plenty of information available on PLA stereocomplex, in this study, we compared neat and PLA stereocomplex properties with various molecular weights in detail. The stereocomplex formation of PLLA and PDLA was prepared by casting the solutions blend of PDLA and PLLA which had various molecular weights. Stereocomplex formation of the blends was evaluated by differential scanning calorimetry (DSC) and wide-angle X-ray diffraction (XRD). Moreover, the mechanical properties of blended and non-blended films were also evaluated and discussed.
2. Experiments

2.1. Materials
Various molecular weights of PLLA (trade name L105, L130 and L175) and PDLA (trade name D120) was received from Total Corbion PLA (Thailand) Ltd. Table 1 summarizes the properties of poly(lactic acid) used in this work. Molecular weights were measured via a Shimadzu RID-10A GPC (Tokyo, Japan) equipped with a reflective index (RI) detector.

| Materials | Trade name | L-unit content (%) | \(M_n\) (kg/mol) | \(M_w\) (kg/mol) | PDI |
|-----------|------------|--------------------|-----------------|-----------------|-----|
| PLLA      | L105       | >99                | 72              | 125             | 1.73|
|           | L130       | >99                | 93              | 180             | 1.93|
|           | L175       | >99                | 113             | 209             | 1.84|
| PDLA      | D120       | <1                 | 89              | 150             | 1.69|

2.2. Processing
Films used for physical measurements were prepared by solution casting. Briefly, each solution of PLLA and PDLA was separately prepared to have a polymer concentration of 1.0 g/dL and then admixed with each other under vigorous stirring in the case of blended film preparation. Chloroform was used as a solvent and the mixing ratio of PLLA and PDLA was fixed at 1:1. The solutions were cast onto petri-dishes, followed by solvent evaporation at room temperature for approximately 3 days and the obtained sample was further vacuum dried to constant weight. Final film thicknesses were approximately 0.4 mm.

2.3. Material Characterization
2.3.1 Differential Scanning Calorimetry (DSC). Homo and stereocomplex melting temperature (\(T_{m1}\) and \(T_{m2}\), respectively) and enthalpy of homo and stereocomplex were determined with a Perkin–Elmer DSC4000 (Massachusetts, USA.) differential scanning calorimeter. Films were heated at the rate of 10°C/min from -10 to 250 °C under a nitrogen gas flow for DSC measurement.

2.3.2 X-ray Diffraction Analysis. X-ray diffraction (XRD) was used to investigate the crystalline structure of the stereocomplex formation (Bruker/D8 Advance BrukerBioSpin AG (Karlsruhe, Germany)). XRD samples were mounted on the XRD platform for analysis. A 2\(^\theta\) range from 2º to 40º in refraction mode was scanned at 2º/min. A computer-controlled wide angle mode goniometer coupled to a sealed tube Cu K\(_\alpha\) line source was filtered with a thin Ni filter.

2.3.3 Mechanical Testing. Tensile properties of films were measured at 25°C and 50% relative humidity using a tensile tester (Texture analyser, TA.XT Plus, Stable Micro System, Surrey, UK.) at cross speed of 2 mm/min. Specimens were cut from the cast films with dimension of 1.5 x 4.5 cm.

3. Results and Discussions
3.1. Thermal Properties
Figure 1 shows the DSC thermogram of 1:1 blend of PLLA (L105, L130 and L175) – PDLA (D120) films. The endothermic peaks noticed from 208 to 230°C can be assigned to the melting peak of stereocomplex crystallites and the melting peak around 175°C was the melting peak of homocrystals (Figure 2) [2, 3]. As can be seen from Table 2, melting temperature (\(T_{m2}\)) and enthalpy of melting (\(\Delta H_m\)) of stereocomplex crystallites was highest as the PDLA blended with lowest molecular weight PLLA (L105). As the molecular weight of PLLA increased, \(T_{m2}\) and \(\Delta H_m\) decreased. When PLLA and PDLA are mixed, the lower molecular weight component may diffuse to the higher molecular weight one, resulting in the nucleation and growth of racemic crystallites. On the other hand, a solution of
PDLA and PLLA, both with a high molecular weight, may not be microscopically homogeneous, resulting in preferential homopolymer crystallization [5, 6].

![Figure 1](image1.png)  **Figure 1.** DSC thermogram of blend films of PDLA and PLLA with various molecular weights.

![Figure 2](image2.png)  **Figure 2.** DSC thermogram of neat PLLA and PDLA film.

**Table 1.** DSC data of blend films of PDLA and PLLA with various molecular weights.

| Samples       | Melting 1 (homocrystal) | Melting 2 (stereocomplex) |
|---------------|-------------------------|---------------------------|
|               | $\Delta H_{m1}$ (J/g)   | $T_{m1}$ (°C)              | $\Delta H_{m2}$ (J/g) | $T_{m2}$ (°C) |
| L105 D120     | 3.7                     | 173.5                     | 47.3                  | 221.9        |
| L130 D120     | 7.3                     | 173.2                     | 26.8                  | 220.3        |
| L175 D120     | 19.0                    | 173.8                     | 17.8                  | 217.6        |

3.2. Wide-Angle X-ray Diffraction
Figure 3 shows XRD profiles of blend films of PDLA and PLLA with various molecular weights measured at room temperature (~25°C). The diffraction peaks at $2\theta = 11.6^\circ$, 20.6°, and 23.5° were assigned to planes of the PLA stereocomplex crystallites (sc) [7-9] and the diffraction peaks located at $2\theta$ about 16.2° and 18.6° corresponded to the α-form homocrystals (Figure 4) [10, 11]. Also, consistent with the DSC result, PDLA (D120) blended with lowest molecular weight PLLA (L105) had highest stereocomplex formation.

![Figure 3](image3.png)  **Figure 3.** WAXD scans of blend films of PDLA and PLLA with various molecular weights.

![Figure 4](image4.png)  **Figure 4.** WAXD scans of neat PLLA and PDLA film.
3.3. Tensile Properties

Figure 5 shows stress-strain curves of PDLA and PLLA with various molecular weights. As evident from Figure 1 and 3, stereocomplex crystallites are the main crystalline species in L105 D120. Although L175 had highest molecular weight and mechanical properties (Figure 6), the tensile strength and Young’s modulus of the blend L175 D120 were lowest. This indicated that increased tensile strength and modulus properties are observed for the blend films containing higher stereocomplex crystallites. It may be reasonable to assume that a higher density of tie chain for stereocomplex samples will result in better mechanical properties [5].

![Figure 5. Stress-strain curves for PDLA/PLLA blend films.](image)

![Figure 6. Stress-strain curves for neat PLLA and PDLA films.](image)

4. Conclusions

In this article, the PDLA and PLLA with various molecular weights were blended by solution cast method. The blend of PDLA and PLLA which had lower molecular weight formed higher stereocomplex crystallites than that having higher molecular weight. Blend films which are rich in stereocomplex crystallites have better tensile strength and modulus than films rich in homo-crystallites.

5. References

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