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Enhanced thermal stability of poly(lactide)s in the melt by enantiomeric polymer blending

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Abstract

Poly(L-lactide) (i.e. poly(L-lactic acid) (PLLA)) and poly(D-lactide) (i.e. poly(D-lactic acid) (PDLA)) and their equimolar enantiomeric blend (PLLA/PDLA) films were prepared and the effects of enantiomeric polymer blending on the thermal stability and degradation of the films were investigated isothermally and non-isothermally under nitrogen gas using thermogravimetry (TG). The enantiomeric polymer blending was found to successfully enhance the thermal stability of the PLLA/PDLA film compared with those of the pure PLLA and PDLA films. The activation energies for thermal degradation (ΔE_{td}) were evaluated at different weight loss values from TG data using the procedure recommended by MacCallum et al. The ΔE_{td} values of the PLLA/PDLA, PLLA, and PDLA films were in the range of 205–297, 77–132, and 155–242 kJ mol^{-1} when they were evaluated at weight loss values of 25–90% and the ΔE_{td} value of the PLLA/PDLA film was higher by 82–110 kJ mol^{-1} than the averaged ΔE_{td} value of the PLLA and PDLA films. The mechanism for the enhanced thermal stability of the PLLA/PDLA film is discussed.

Keywords: Polylactide; Thermal stability; Enantiomeric polymer blending

1. Introduction

Biodegradable polyesters are being investigated as an alternative to more conventional non-degradable or slowly degrading synthetic polymers in order to reduce their impact on the environments. Among the family of biodegradable polyesters, polylactides (i.e. poly(lactic acid)s (PLA)) have been attracting much attention because they are producible from renewable resources such as starch, biodegradable and compostable, and have very low or non-toxicity and high mechanical performance comparable to those of commercial polymers [1–12]. However, thermal stability of PLAs is not sufficiently high to some applications as an alternative of commercial polymers.

Thermal processes such as melt molding and spinning cause thermal degradation of PLAs. Gupta and Deshmukh [13,14] studied thermal oxidative degradation of PLA and reported that the first order random decomposition of PLA occurs under an isothermal condition and the activation energy for thermal oxidation to be 105–126 kJ mol^{-1}. On the other hand, Jamshidi et al. [15], Babanalbandi et al. [16], and Lee et al. [17] revealed that the terminal groups play an important role to decrease the molecular weight, forming low molecular weight cyclic monomer and oligomers. McNeill and Leiper [18,19], Kopinke and Mackenzie [20, 21], and Waschsen et al. [22,23] investigated in detail the thermal degradation mechanisms (non-radical and radical mechanisms) of poly(DL-lactide) (i.e. poly(DL-lactic acid) (PDLLA)) [18,19] and poly(L-lactide) (i.e. poly(L-lactic acid) (PLLA)) [20–23] for a wide temperature range from ambient temperature to ca. 450 °C. Kopinke et al. concluded that the first peak at 295 °C in DTG curve in non-purified PLLA can be attributed to a tin-catalyzed depolymerization which yields exclusively lactide, while the second peak (350 °C) is due to several non-catalytic decomposition of which main products are carbon oxides, acetaldehyde, lactide, and further cyclic oligomers up to nine units [21]. McNeill and Leiper [19] and Babanalbandi et al. [16] evaluated the activation energies for thermal degradation (ΔE_{td}) of PDLLA and PLLA to be 119 and 72–103 kJ mol^{-1}, respectively. On the other hand, Day et al. [24] and Aoyagi et al. [25] carried out comparative studies

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on thermal degradation of the biodegradable polyesters including PLLA.

Some additives as catalyst deactivators have been reported to stabilize PLAs in the melt. Such additives include benzoyl peroxide (Södergård and Näsman) [26,27], 1,4-dianthraquinone (McNeill and Leiper) [18,19], 2-hydroxy-2,4,6-cycloheptatrienone (Tropolone) (Wachsen et al.) [22], natural and biodegradable acid (Hartmann) [28]. Zhang et al. [29] and Cam and Marucci [30] claimed that the factors affecting the thermal degradation of PDLLA and PLLA are polymerization conditions and the lactide contents, respectively, while McNeill and Leiper [18,19] and Jamshidi et al. [15] reported that the acetylation of hydroxyl terminal group enhances the thermal stability of PLAs.

On the other hand, Ikada et al. [31] found that a stereocomplex is formed from enantiomeric PLAs, PLLA and poly(D-lactide) (i.e. poly(D-lactic acid) (PDLA)) due to the peculiar strong interaction between PLLA and PDLA chains. The stereocomplexed PLLA/PDLA blend has melting temperature (T_m) (220–230 °C) by ca. 50 °C higher than those of pure PLLA and PDLA (170–180 °C) [31] and can retain a non-zero strength in the temperature range up to the melting temperature (230 °C) [32]. Moreover, the PLLA/PDLA blend has a higher hydrolysis-resistance compared with that of the pure PLLA and PDLA even when it is amorphous-made, due to the peculiar strong interaction between PLLA and PDLA chains [33,34]. On the basis of these findings, enantiomeric polymer blending is expected to enhance the thermal stability of the PLLA/PDLA blend in the melt compared with those of the pure PLLA and PDLA. However, as far as we know, such enhancement of thermal stability of optically active polymers in the melt by enantiomeric polymer blending has not been reported so far.

The purposes of this study are to investigate the thermal degradation behavior of the PLLA, PDLA, and their equimolar blend in the melt, and to elucidate the effects of enantiomeric polymer blending on the thermal stability and degradation. For these purposes, PLLA and PDLA having similar molecular weights were synthesized and their pure and equimolar blend films were prepared. The thermal degradation behavior of these films was investigated isothermally and non-isothermally using thermogravimetry (TG).

2. Experimental section

2.1. Materials

PLLA and PDLA were synthesized by ring-opening polymerization of L- and D-lactide, respectively, in bulk at 140 °C for 10 h using stannous octoate (0.03 wt%) and lauryl alcohol as a catalyst and an initiator, respectively [35,36]. The synthesized polymers were purified by precipitation using methylene chloride and methanol, as a solvent and a non-solvent, respectively. The purified polymers were dried in vacuum for at least 1 week before film preparation. The pure PLLA and PDLA films and their equimolar enantiomeric blend films were prepared by casting 1 g dl^{-1} solutions of the polymers using methylene chloride as a solvent and subsequent rapid solvent evaporation at room temperature (25 °C) for about 1 day [33,34]. For preparation of the enantiomeric blend film from PLLA and PDLA, the individual solutions of PLLA and PDLA were prepared in advance and then mixed with each other before casting. The as-cast films were dried in vacuum for 1 week before molecular characterization and thermal measurements. In this study, L, D, and L/D stand for pure PLLA and PDLA films and their 1:1 blend film, respectively.

2.2. Measurements

The weight- and number-average molecular weights (M_w and M_n, respectively) and the molecular weight distribution of the films were evaluated in chloroform at 40 °C by a Tosoh GPC system (refractive index monitor: RI-8020) with TSK Gel columns (GMH$_{XL}$ × 2) using polystyrene as a standard. The specific optical rotation ($[\alpha]^{25}_{589}$) values of polymers were measured using a JASCO DIP-140 polarimeter in chloroform at 25 °C at a wave length of 589 nm. The $[\alpha]^{25}_{589}$ values of PLLA and PDLA, -154 and 155 deg dm^{-1} g^{-1} cm^3 are, respectively, in good agreement with reported values [35,36].

The glass transition and melting temperatures of homo- and stereocomplex crystallites (T_g, $T_{m,H}$, and $T_{m,S}$, respectively) and the crystallinities of homo- and stereocomplex crystallites ($x_{c,H}$ and $x_{c,S}$, respectively) of the films were determined by differential scanning calorimetry using a Shimadzu DT-50 according to a procedure reported earlier [32–36]. In this evaluation, the values of 135 and 142 (J g^{-1} of polymer) were used as the enthalpies of melting of the homo- (PLLA or PDLA) and the stereocomplex crystals, respectively, having an infinite crystal thickness as reported by Miyata and Masuko [37] and by Loomis et al. [38] and ourselves [39]. Here, homo-crystallites are composed of either PLLA or PDLA chains, while in stereocomplex crystallites equimolar PLLA and PDLA are packed side by side [8–10,12,40,41]. The molecular characteristics and properties of the films used in this study are summarized in Table 1.

The thermal degradation behavior of the films (sample weight of ca. 3 mg) was observed by TG using a Shimadzu DTG-50 under a nitrogen gas flow of 50 ml min^{-1}. The weight losses of the specimens were measured isothermally under the constant holding temperatures (250–270 °C) or non-isothermally with heating at a constant rate of 10 °C min^{-1} up to 400 °C. The holding temperatures of 250–270 °C were selected because the T_m of PLA stereocomplex was 225 °C (Table 1) and the degradation mechanism is reported to change at the temperature exceeding 270 °C [19].

Table 1
Characteristics and properties of as-cast L, D, and L/D films

Code	Init. conc.[a] (wt%)	M_n (g mol^{-1})	M_w/M_n	$[\alpha]^{25}_{589}$ (deg dm^{-1} g^{-1} cm^3)	T_g (°C)	$T_{m,H}$[b] (°C)	$T_{m,S}$[c] (°C)	$T_{d,S}$[d] (°C)	$T_{d,E}$[e]	$x_{c,H}$[f]	$x_{c,S}$[g]
L[h]	0.5	8.7×10^4	1.8	−154	66	177	–	297	362	34	–
D[i]	0.4	9.5×10^4	1.8	+155	66	178	–	287	361	36	–
L/D[j]	–	9.4×10^4	1.6	–	67	177	225	292	363	7	35

[a] Initiator (lauryl alcohol) concentration for polymerization.
[b] Melting temperature of homo-crystallites.
[c] Melting temperature of stereocomplex crystallites.
[d] Starting temperature for non-isothernmal degradation.
[e] Ending temperature for non-isothernmal degradation.
[f] Crystallinity of homo-crystallites.
[g] Crystallinity of stereocomplex crystallites.
[h] Poly(L-lactide) (PLLA) film.
[i] Poly(D-lactide) (PDLA) film.
[j] Equimolar blend film of PLLA and PDLA.

3. Results and discussion

3.1. Non-isothermal degradation

The percentage remaining weight of the films measured non-isothermally at the constant temperature rise is shown in Fig. 1 as a function of temperature. On the basis of the reported results that the terminal groups play an important role for thermal degradation [15–17], the D film having a higher molecular weight was expected to have a higher thermal stability than that of the L film having a lower molecular weight. However, the D film showed a shorter induction period for a significant weight loss compared with that of the L film. It is plausible that the D film contains a higher amount of tin catalyst and/or lactide remaining after the purification by precipitation, which may have enhanced the thermal degradation of the D film at the temperature exceeding 290 °C, as reported earlier [15,18,19,22,26–28,30]. The L/D film showed mean weight loss behavior between those of the L and D films at the temperature below 350 °C, while the remaining weight of the L/D film became the highest among the films at the temperature exceeding 350 °C. The latter finding suggests that the thermal stability of the L/D film was higher than those of the L and D films.

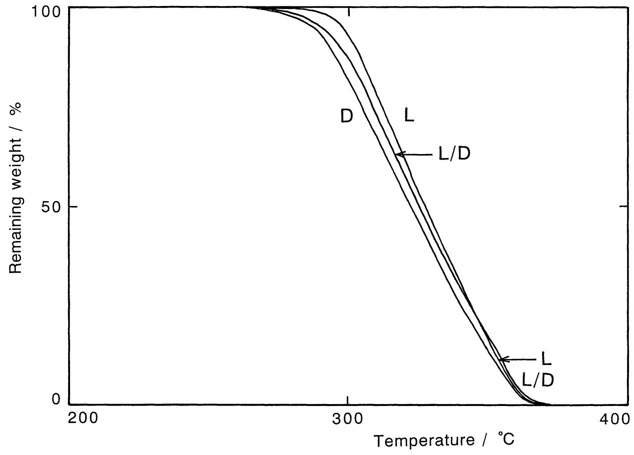

Fig. 1. The percentage remaining weight of the films measured non-isothermally at the constant heating rate as a function of temperature.

The starting and ending temperatures ($T_{d,S}$ and $T_{d,E}$, respectively) for the thermal degradation of the films were evaluated from extrapolation of the straight line parts of the degradation curves to remaining weights of 100 and 0%, respectively, as schematically depicted by Cam and Marucci in the literature [30]. The evaluated values are listed in Table 1. The $T_{d,S}$ values of the films were in the range of 287–297 °C and became higher in the following order: D film < L/D film < L film, while the $T_{d,S}$ values of the films was very similar with each other (361–363 °C). These $T_{d,S}$ and $T_{d,E}$ values obtained in this study were very similar to previously reported values [15,18,20,21,24,25].

3.2. Isothermal degradation

To investigate in detail with respect to the thermal degradation behavior and stability, we performed the isothermal measurements at constant holding temperatures of 250–270 °C. Fig. 2 shows the percentage remaining weight of the films at different holding temperatures as a function of degradation time. At 250 °C the remaining weights of the L and D films started to decrease without any induction periods and then decreased monotonically to zero at 120 min and to 4% at 200 min, while that of the L/D film started to decrease after ca. 40 min of induction period and then decreased gradually to 23% at 200 min. It is interesting to note that the remaining weight of the D film was higher than that of the L film for all the degradation time in marked contrast with the results in non-isothermal measurements in which actual degradation occurred at the temperature exceeding 290 °C. This result can be explained as follows; the D film had the higher initial molecular weight than the L film and therefore the D film had a lower amount of terminal groups where cyclic oligomers and monomers are formed, resulting in a higher remaining weight compared with that of the L film.

At 260 °C the L/D film showed the highest remaining

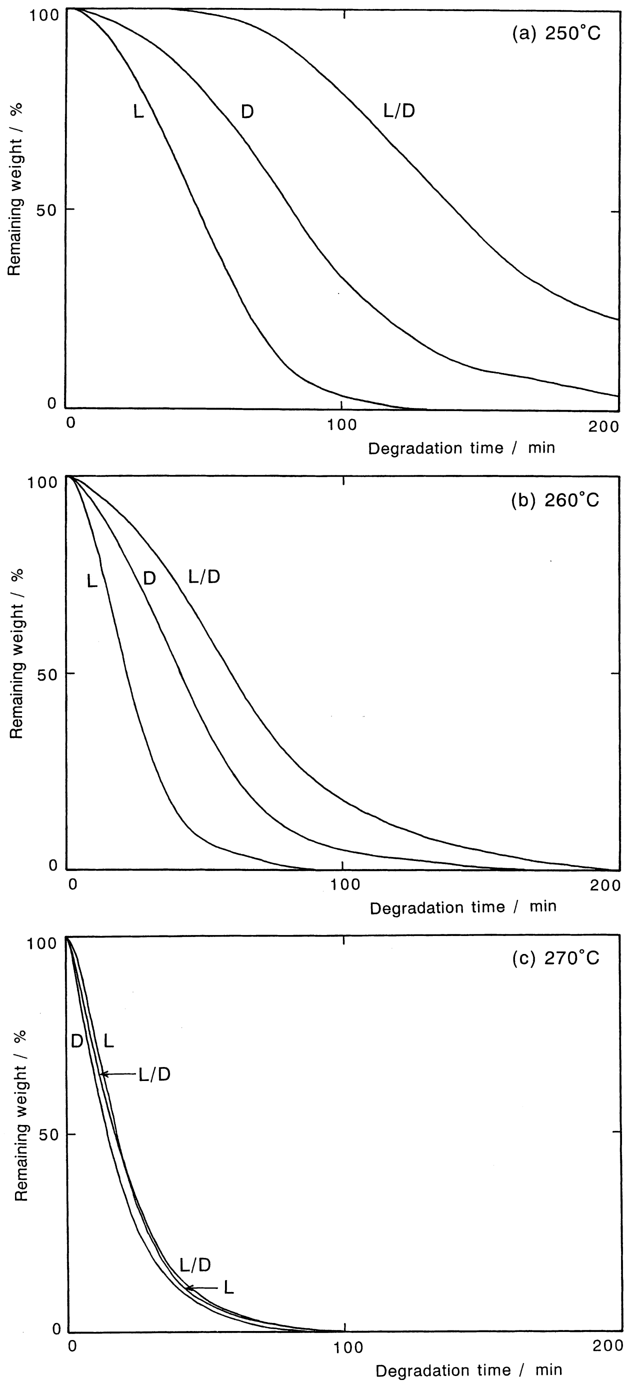

Fig. 2. The percentage remaining weight of the films measured isothermally at (a) 250 °C, (b) 260 °C, and (c) 270 °C as a function of degradation time.

weight among the films for the degradation period studied here, although the difference between weight loss behavior of the films became smaller than that at 250 °C. At 270 °C the L/D film gave the intermediate weight loss behavior between that of the L and D films in the first 20 min, while the weight loss of the L/D film became the highest among the films in the degradation periods exceeding 20 min. This is very similar to that obtained non-isothermally at the constant of temperature rise. The result obtained here reveals that the thermal stability of the L/D film was enhanced by the enantiomeric polymer blending at the temperature below 260 °C. The lowest remaining weight of the D film at 270 °C among the films can be ascribed to the higher amount of tin catalyst after purification in the D film compared with those of the other films, which may have enhanced its thermal degradation when the degradation temperature approached 295 °C [21].

The degradation time (t) required to give fixed weight losses (25, 50, 75, and 90%) were evaluated form Fig. 2 and depicted in Fig. 3 as a function of reciprocal of degradation temperature (T). Evidently, the logarithmic t increased linearly with T^{-1} and was higher for the L/D film than for the L and D films at 250 and 260 °C, while was similar with each other at 270 °C. At 250 °C ($1000T^{-1} = 1.912\ \mathrm{K}^{-1}$) the t value required to give a certain weight loss of the L/D film was 2.9–3.4 and 1.7 × 1.9 times that of the D and L films, respectively, while at 260 °C ($1000T^{-1} = 1.876\ \mathrm{K}^{-1}$) it was 2.7–2.8 and 1.4–1.5 times that of L and D films, respectively. These findings confirm that the enantiomeric polymer blending enhances the thermal stability of the L/D film at the temperature below 260 °C.

To calculate the ΔE_{td} values, we used the procedure recommended by MacCallum et al. [42–46] and utilized successfully by Babanalbandi et al. [16]. The t (min) for a weight loss X (wt%) can be expressed as a function of degradation temperature T (K) using the following equation:

$$\ln t = \ln[F(1 - X/100)] - \ln A + \Delta E_{\mathrm{td}}/RT \qquad (1)$$

where $F(1 - X/100)$ is an undefined function of X and A is a constant.

The ΔE_{td} values obtained using Eq. (1) were reported to vary depending on the weight loss [16]. Therefore, in this study, ΔE_{td} values were evaluated from Fig. 3 for different weight loss values in the range of 25–90% using Eq. (1) and the obtained results are shown in Fig. 4 as a function of weight loss. The ΔE_{td} values of the L/D, L, and D films decreased with the weight loss and were in the ranges of 205–297, 77–132, and 155–242 kJ mol^{-1}, respectively. The obtained ΔE_{td} values of the L films are comparable with the ΔE_{td} values reported for PLLA (72–103 kJ mol^{-1} (Babanalbandi et al.) [16], 110 kJ mol^{-1} (Kopinke et al.) [20], and 80–160 kJ mol^{-1} (Aoyagi et al.) [25]) and for PDLLA (119 kJ mol^{-1} (McNeill and Leiper) [19]). However, those of the L/D and D films are, respectively, much and slightly higher than the above mentioned values for PLLA and PDLLA. The larger ΔE_{td} value of the D film compared with that of the L film can be attributed to the enhancement of thermal degradation of the D film probably due to the higher amount of catalyst, which became stronger with approaching 295 °C [21] and thereby resulted in the seemingly larger ΔE_{td} value of the D film.

The ΔE_{td} value of the L/D film was higher than those of the L and D films when compared at the same weight loss and the difference between the ΔE_{td} value of the L/D film

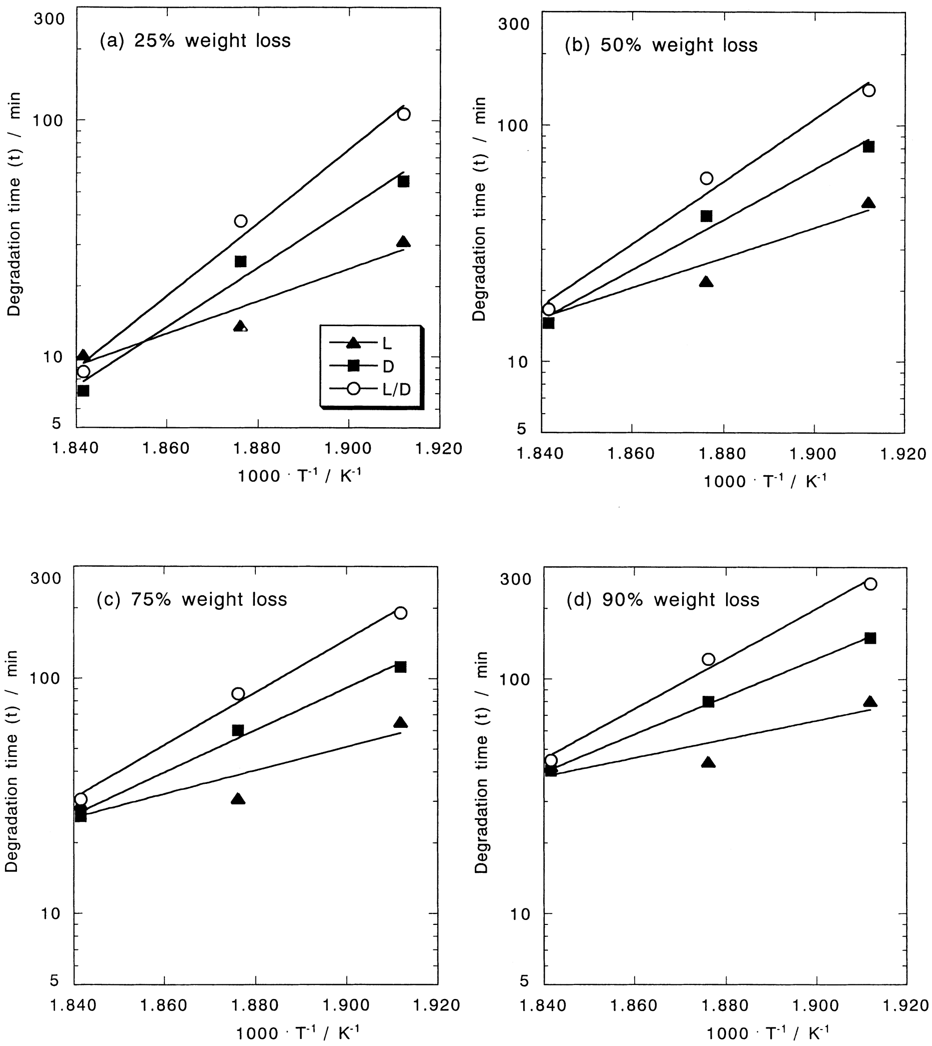

Fig. 3. The degradation time (t) required to give fixed weight losses as a function of T^{-1} : weight loss = (a) 25%, (b) 50%, (c) 75%, and (d) 90%.

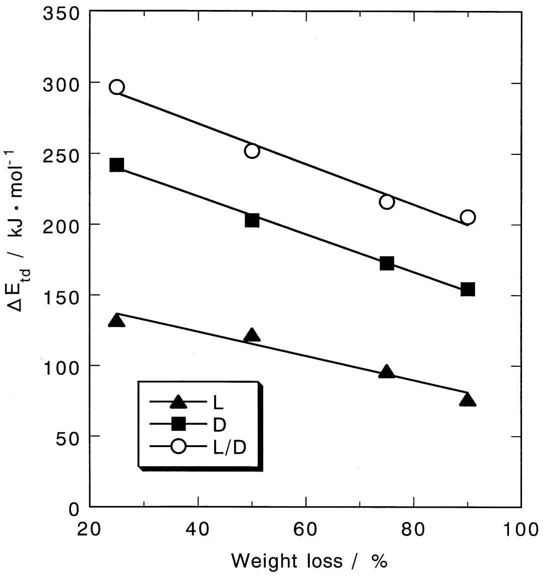

Fig. 4. The ΔE_{td} of the films as a function of weight loss.

and the averaged ΔE_{td} value of the L and D films was in the range of 82–110 kJ mol^{-1}. This again confirms that the thermal stability of the L/D film was enhanced by the enantiomeric polymer blending. The highest ΔE_{td} value of the L/D film can be ascribed to the peculiar strong interaction between PLLA and PDLA chains in the film even when they are in the melt, which decreases the mobility of the chains and thereby retards the thermal degradation of the film. The peculiar strong interaction between PLLA and PDLA chains was suggested by the higher hydrolysis-resistance of the amorphous-made PLLA/PDLA blend film in the phosphate-buffered solution compared with those of the amorphous-made pure PLLA and PDLA films [34].

The peculiar interaction between PLLA and PDLA chains may arise from their 10_3 or 3_1 helical conformation as in the crystallized state [40,41], even when they are in the melt. In such helical states, the interaction between the left and right handed helixes of PLLA and PDLA in their blend film must be stronger than that between the chains having the same helical direction in pure PLLA and PDLA, resulting in the decreased chain mobility and the enhanced thermal stability of the L/D film at the temperature below 260 °C. With an increase in temperature, the helical chains are expected to be transformed to random-coil chains, in which the interaction between PLLA and PDLA chains is similar to that between PLLA chains or PDLA chains. Accordingly, at the temperature exceeding 260 °C, the difference in thermal stability between the pure and the blend films is expected to become insignificant. However, further investigations are required to elucidate the mechanism for the enhancement of thermal stability of the enantiomeric blend film.

In conclusion, at the temperature below 260 °C the enantiomeric polymer blending successfully enhanced the thermal stability of the L/D film compared with that of the pure L and D films. In other words, the thermal stability of PLLA can be improved by the addition of its enantiomer PDLA and vice versa. The ΔE_{td} value of the L/D film was in the range of 205–297 kJ mol^{-1}, which was higher by 82–110 kJ mol^{-1} than the averaged ΔE_{td} value of the L and D films.

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