

Preparation of chain-extended stereocomplex PLLA-PEG-PLLA/PDLA-PEG-PDLA blends for potential use as flexible and high heat-resistant bioplastics

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Abstract:

Stereocomplex poly(lactides) (scPLAs) bioplastics show better heat resistance than the poly(L-lactide) (PLLA). However scPLAs have low flexibility. In this research, flexible poly(L-lactide)-*b*-poly(ethylene glycol)-*b*-poly(L-lactide)/poly(D-lactide)-*b*-poly(ethylene glycol)-*b*-poly(D-lactide) (PLLA-PEG-PLLA/PDLA-PEG-PDLA) blends with chain extension were prepared by melt process. The effect of blend ratios on thermal, mechanical and heat-resistant properties of chain-extended blends were determined. The blends exhibited faster crystallization upon cooling process than the pure PLLA-PEG-PLLA. PLA-stereocomplex crystallinities and heat resistance of the blends increased steadily and strain at break decreased as increasing the PDLA-PEG-PDLA ratio.

Keywords: Poly(lactide), block copolymers, stereocomplex, chain extension, heat resistance

I. INTRODUCTION

Poly(L-lactic acid) or poly(L-lactide) (PLLA) has received extensive attention in applications of medical devices and packaging to gradually replace oil-based plastics. This is due to its bio-renewability, low toxicity, biodegradability and good processability [1]. However, poor heat-resistance and brittleness of PLLA are the main disadvantages to limit its widespread application [2, 3]. PLLA products with high heat-resistance are appropriate for some applications such as microwave applications and heat-treatment/hot-fill packaging, etc.

PLLA/poly(D-lactide) (PDLA) blends called as stereocomplex poly(lactides) (scPLA) exhibited better heat and hydrolysis resistance than did PLLA [4, 5]. The intermolecular forces in stereocomplex crystallites of scPLA were stronger than in the homo-crystallites of PLLA [4–7]. This induced faster crystallization rate and higher melting temperature (T_m) of the

scPLA than the PLLA. The higher-crystallinity scPLA enhanced its heat resistance [2]. However, the scPLA had a glass transition temperature (T_g) similar to the PLLA. The low flexibility of scPLA still limits it in some applications.

Poly(ethylene glycol) (PEG) have been used as an initiators for ring-opening polymerization of L-lactide monomer to prepare PLLA-PEG-PLLA triblock copolymers [8, 9]. These PLLA-PEG-PLLA exhibited greater flexibility than PLLA due to the PEG middle-blocks acted as plasticizers. Moreover, the PLLA-PEG-PLLA also showed faster crystallization than the PLLA [8]. Chain extension of PLLA-PEG-PLLA produced long-chain branching structures that improved its film strength and extensibility [9]. However, poor heat-resistance of these PLLA-PEG-PLLA was still found.

In recent years, PDLA-PEG-PDLA triblock copolymers have been blended with PLLA to form high flexible stereocomplex PLLA/PDLA-PEG-PDLA [10–16]. The heat resistance of the PLLA/PDLA-PEG-PDLA blends has been not evaluated. The PLLA-PEG-PLLA/PDLA-PEG-PDLA blends have also fabricated by both solution [17] and melt blending [18]. The stereocomplex crystallinities and heat resistance of the PLLA-PEG-PLLA/PDLA-PEG-PDLA blends were improved by increasing the PDLA-PEG-PDLA ratio. However chain extension of PLLA-PEG-PLLA/PDLA-PEG-PDLA blends has not been reported so far. In this work, chain-extended PLLA-PEG-PLLA/PDLA-PEG-PDLA blends were prepared by melt blending. Their stereocomplexation, mechanical properties and heat resistance were investigated and discussed.

II. EXPERIMENTAL

A. Materials

PLLA-PEG-PLLA and PDLA-PEG-PDLA triblock copolymers were synthesized by ring-opening polymerization of L-lactide and D-lactide, respectively, as described in our

previous work [9, 18]. PEG (M.W. = 20,000 g/mol, Sigma-Aldrich, Switzerland) was used as an initiator and stannous octoate (Sigma-Aldrich, Switzerland) was used as a catalyst for polymerization of triblock copolymers. The number-average molecular weight (M_n) of PLLA-PEG-PLLA and PDLA-PEG-PDLA from gel permeation chromatography (GPC) were 90,000 and 85,400 g/mol, respectively, while the dispersity index (DI) were 2.8 and 2.1, respectively. Joncryl® chain extender (ADR 4368, BASF, Thailand) were used as received. All reagents in analytical grade were used.

B. Preparation of chain-extended PLLA-PEG-PLLA/PDLA-PEG-PDLA blends

The chain-extended PLLA-PEG-PLLA/PDLA-PEG-PDLA blends were prepared by melt blending at 200°C for 4 min with a rotor speed of 100 rpm using an internal mixer (HAAKE PolyLab OS Rheomex). The copolymers and Joncryl® were dried under vacuum at 50°C overnight prior to the melt blending. The Joncryl® content was 4.0 phr. The PLLA-PEG-PLLA/PDLA-PEG-PDLA weight ratios were 100/0, 90/10, 80/20, 70/30 and 60/40. The obtained blends were pelletized into small pieces (~5 mm). The blend films with 0.2 – 0.3 mm in thicknesses were prepared at 240°C without any force for 1.0 min followed with a compression force of 5.0 ton for 1.0 min using a compression molding machine (Auto CH Carver).

C. Characterization of chain-extended PLLA-PEG-PLLA/PDLA-PEG-PDLA blends

The thermal properties of the chain-extended PLLA-PEG-PLLA and blends were characterized by a differential scanning calorimeter (DSC, Perkin-Elmer model Pyris Diamond) under nitrogen gas flow. For each DSC heating scan, sample was firstly melted at 250°C for 2 min in order to erase the thermal history, after which was quenched to 0°C before reheating from 0 to 250°C with a rate of 10°C/min. For each DSC cooling scan, the sample was firstly melted at 250°C for 2 min in order to erase the thermal history before cooling from 250°C to 0°C at a rate of 10°C/min.

The crystal structures of the chain-extended PLLA-PEG-PLLA and blend films were investigated from wide-angle X-ray diffractometry (XRD) spectra which were recorded on a XRD spectrometer (Bruker model D8 Advance). The range of 2θ from 5° to 30° was scanned at 3°/min with a CuK α radiation. The XRD was operated at 40 kV and 40 mA. The degrees of crystallinity from XRD ($X_{c,XRD}$) for PLA-homo-crystallites (hc- $X_{c,XRD}$) (Eq. 1) and PLA-stereocomplex crystallites (sc- $X_{c,XRD}$) (Eq. 2) were estimated [19].

$$hc-X_{c,XRD} (\%) = S_{hc}/(S_{hc} + S_{sc} + S_a) \times 100 \quad (1)$$

$$sc-X_{c,XRD} (\%) = S_{sc}/(S_{hc} + S_{sc} + S_a) \times 100 \quad (2)$$

where S_{hc} , S_{sc} and S_a are the integrated intensity peaks for homo-crystallites and stereocomplex crystallites as well as the integrated intensity of the amorphous halo, respectively.

The tensile tests of blend films with 100 × 10 mm in size were conducted on an Universal Mechanical Tester (Lloyds model LRX+) under a tensile speed of 50 mm/min at 25°C. A gauge length was 50 mm. Data analysis was averaged on at least five determinations of each blend film.

The thermo-mechanical property of blend films with 5 × 20 × 0.2 mm in size was performed on a dynamic mechanical analyzer (DMA, TA Instruments model Q800) at a frequency of 1 Hz and a amplitude of 10 μ m. The temperature sweep was heated from 30 to 150°C at 2°C/min.

The dimensional stability to heat of blend films with 5 × 40 × 0.2 mm in size was performed by hanging into an air oven (80°C) for 30 sec under a 200 g load. Initial length of films was 20 mm. The dimensional stability to heat was estimated from the following equation [20].

$$\text{Dimensional stability to heat (\%)} = [\text{initial length (mm)}/\text{final length (mm)}] \times 100 \quad (3)$$

III. RESULTS AND DISCUSSION

A. Stereocomplexation

Figure 1 shows DSC heating curves of chain-extended PLLA-PEG-PLLA and blends. The T_g of the chain-extended PLLA-PEG-PLLA was 34°C [Figure 1(a)]. The T_g s of the chain-extended blends were in range 36–38°C [Figures 1(b)–1(e)]. The cold-crystallization temperatures (T_{cc}) of the chain-extended blends (83–117°C) exhibited at higher temperature than the chain-extended PLLA-PEG-PLLA (74°C). We attribute this to restriction of chain mobility for glassy-to-rubbery transition and cold crystallization by stronger intermolecular interactions between PLLA and PDLA end-blocks of the blends.

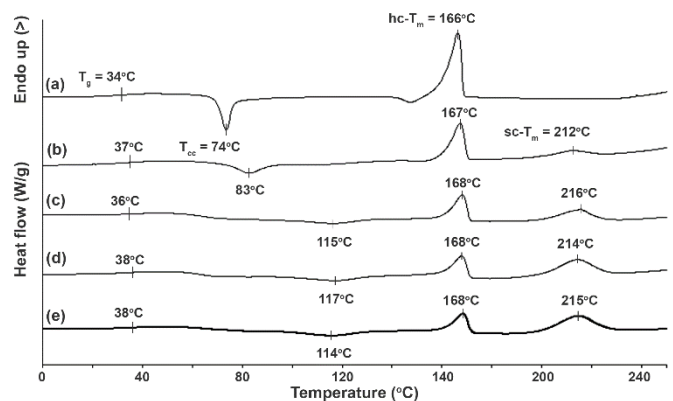


Figure 1: DSC heating curves of chain-extended blends with PLLA-PEG-PLLA/PDLA-PEG-PDLA weight ratios of (a) 100/0, (b) 90/10, (c) 80/20, (d) 70/30 and (e) 60/40 (T_g , T_{cc} , hc- T_m and sc- T_m peaks as shown).

The enthalpies of cold crystallization (ΔH_{cc}), of homo-crystalline melting (hc- ΔH_m) and of stereocomplex-crystalline melting (sc- ΔH_m) from Figure 1 are summarized in Table 1. It

was found that the ΔH_{cc} and $hc-\Delta H_m$ values decreased gradually and the $sc-\Delta H_m$ increased steadily with increasing PLLA-PEG-PDLA ratio. The increasing $sc-\Delta H_m$ indicates that the stereocomplexation was enhanced. The T_m for homo-crystallites ($hc-T_m$) and stereocomplex crystallites ($sc-T_m$) were in the ranges 166–168°C and 212–216°C, respectively. The X_c from DSC could not be determined due to overlapping of cold-crystallization peaks of homo- and stereocomplex crystallites.

Table 1: Thermal properties of chain-extended PLLA-PEG-PLLA and blends.

PLLA-PEG-PLLA/PDLA-PEG-PDLA (w/w)	ΔH_{cc} (J/g)	$hc-\Delta H_m$ (J/g)	$sc-\Delta H_m$ (J/g)
100/0	19.6	41.0	-
90/10	11.6	24.1	6.8
80/20	7.9	18.9	15.9
70/30	7.7	18.1	25.9
60/40	7.5	14.5	26.7

DSC cooling curves of the PLLA-PEG-PLLA and blends are shown in Figure 2. The PLLA-PEG-PLLA had a crystallization temperature (T_c) at 90.9°C with a enthalpy of crysallization (ΔH_c) of 18.9 J/g [Figure 2(a)]. The T_c and ΔH_c values of the blends significantly increased when the PDLA-PEG-PDLA ratio was increased up to 20 wt%. The increasing T_c indicates that crystallization occurs faster. The higher ΔH_c implies increment of crystallization. Therefore crystallization of the blends accerelated during cooling scan by increasing the PDLA-PEG-PDLA ratio. It has been reported that the crystallization of stereocomplex crystallites of PLLA/PDLA blends was faster than the homo-crystallites of PLLA [4]. In addition, the chain-extended blends exhibited faster crystallization than the non-chain-extended blends for the same blend ratio [18].

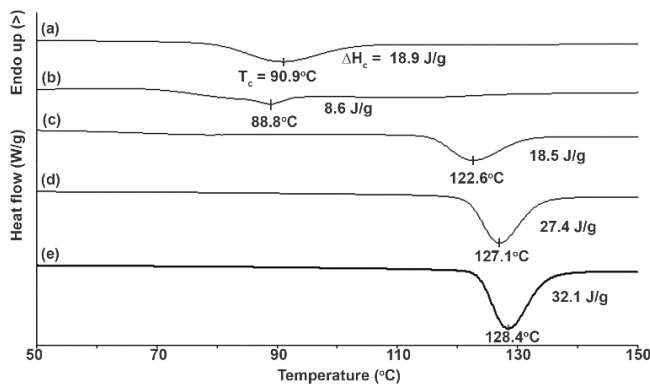


Figure 2: DSC cooling curves of chain-extended blends with PLLA-PEG-PLLA/PDLA-PEG-PDLA weight ratios of (a) 100/0, (b) 90/10, (c) 80/20, (d) 70/30 and (e) 60/40 (T_c peaks and ΔH_c values as shown).

B. Crystal structures

Figure 3 illustrates XRD spectra of chain-extended PLLA-PEG-PLLA and blend films. The PLLA-PEG-PLLA film did not show any XRD peaks attributable to completely amorphous states. The long-chain branching structures of chain-extended PLLA-PEG-PLLA inhibited crystallization of PLLA end-blocks [9]. All the blend films exhibited only stereocomplex-crystalline structure with XRD peaks at 12°, 21° and 24° [19, 20] without any homo-crystalline structure. This suggests the compression molding enhanced stereocomplexation of chain-extended blend films.

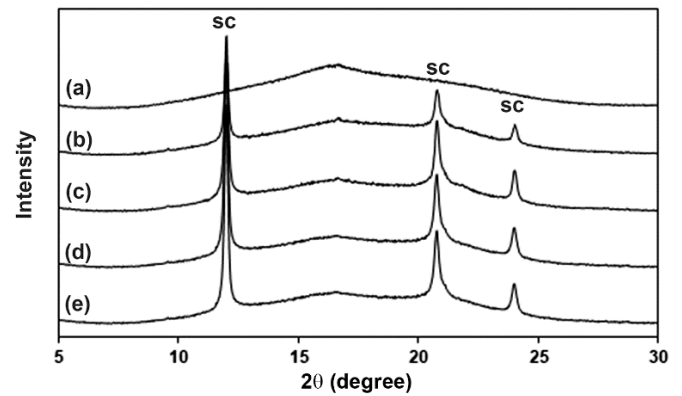


Figure 3: XRD spectra of chain-extended blend films with PLLA-PEG-PLLA/PDLA-PEG-PDLA weight ratios of (a) 100/0, (b) 90/10, (c) 80/20, (d) 70/30 and (e) 60/40.

The $hc-X_{c,XRD}$ and $sc-X_{c,XRD}$ of blend films are reported in Table 2. The $sc-X_{c,XRD}$ of films increased with increasing the PDLA-PEG-PDLA ratio according to the increased $sc-\Delta H_m$ values from DSC. It should be noted that the chain-extended blend films had higher $sc-X_{c,XRD}$ than the non-chain-extended blend films as reported in our previous work [18]. This indicates the branching structures of chain-extended blend films enhanced stereocomplexation between PLLA and PDLA end-blocks. More free-volume of branching structures may enhance chain mobility for stereocomplex crystallization.

Table 2: XRD results of chain-extended PLLA-PEG-PLLA and blend films.

PLLA-PEG-PLLA/PDLA-PEG-PDLA (w/w)	$hc-X_{c,XRD}$ (%) ^a	$sc-X_{c,XRD}$ (%) ^b
100/0	-	-
90/10	-	15.1
80/20	-	26.5
70/30	-	27.2
60/40	-	28.5

^a calculated from equation (1).

^b calculated from equation (2).

C. Tensile properties

The tensile testing are used to examine the mechanical properties of chain-extended PLLA-PEG-PLLA and blend films, as shown in Figure 4. The films had stress at break in range 15–18 MPa. The strain at break of the films significantly decreased with increase in the ratio of PDLA-PEG-PDLA. This may be explained by the increment of film crystallinities reducing film extensibility. However, the strain at break of all the blend films was still higher than with pure PLLA films (3–5%). Thus these blend films were more flexible than the PLLA films.

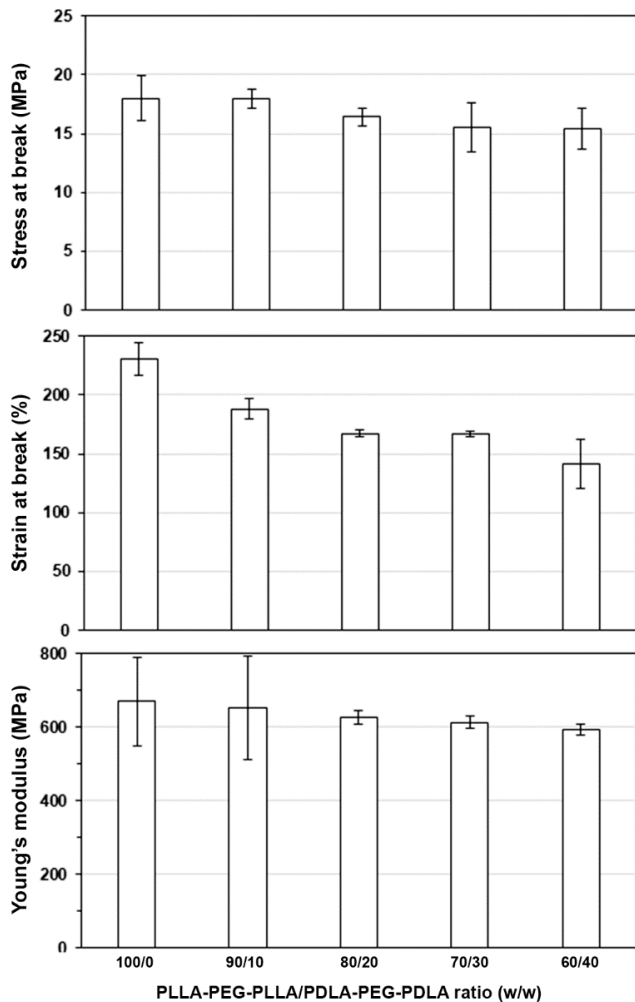


Figure 4: Tensile properties of chain-extended blend films with various PLLA-PEG-PLLA/PDLA-PEG-PDLA weight ratios.

From our previous work, the strain at break of non-chain-extended PLLA-PEG-PLLA/PDLA-PEG-PDLA blend films increased steadily with increase in the PDLA-PEG-PDLA ratio [18]. The $sc-X_{c,XRD}$ of non-chain-extended blend films were in range 2–5%. The interactions between PLLA and PDLA end-blocks in an amorphous phase enhanced film extensibility. However, in this work, chain-extension reaction induced more $sc-X_{c,XRD}$ (15–28%) of the blend films. A decrease in strain at break of chain-extended blend films was then found when the

PDLA-PEG-PDLA ratio and $sc-X_{c,XRD}$ were increased. The Young's modulus of blend films were in ranges 593–670 MPa.

D. Heat resistance

The DMA method have been widely used to determine heat resistance of PLLA and scPLA [21–24]. The storage modulus of low-crystallinity PLLA largely dropped as the temperature passed the T_g region due to its rubber-like character before a large rise due to cold-crystallization of PLLA during DMA heating scan. This indicates that low-crystallinity PLLA had poor heat-resistance [24]. Meanwhile high heat-resistance was obtained when the PLLA had a higher degree of crystallinity which maintains stiffness of PLLA during passing the T_g region [21]. A smaller decrease storage modulus of high heat-resistant PLLA in T_g region was obtained.

Figure 5 shows storage modulus of blend films. The storage modulus dramatically dropped with increasing temperature before rising up again in range 90–130°C due to cold crystallization of PLLA and PDLA end-blocks. The cold-crystallization regions of the blend films were found at higher temperature than the PLLA-PEG-PLLA film and shifted to higher temperature ranges as increase in the PDLA-PEG-PDLA ratio according to the T_{cc} changes from DSC as described above. This could be explained by the chain mobility of copolymers during cold crystallization being restricted and with the interactions between PLLA and PDLA end-blocks [18]. The PLLA-PEG-PLLA film exhibited the increase of storage modulus (see black line in Figure 5). This curve style indicates poor heat-resistance of this PLLA-PEG-PLLA film [21, 24]. The increases of storage modulus of the blend films were less than the PLLA-PEG-PLLA film and steadily decreased as the PDLA-PEG-PDLA ratio increased. This suggests the higher PDLA-PEG-PDLA ratios suppressed cold-crystallization effects according to the ΔH_{cc} results from DSC as described above. This is due to the blend films with higher PDLA-PEG-PDLA ratios having higher $sc-X_{c,XRD}$ values.

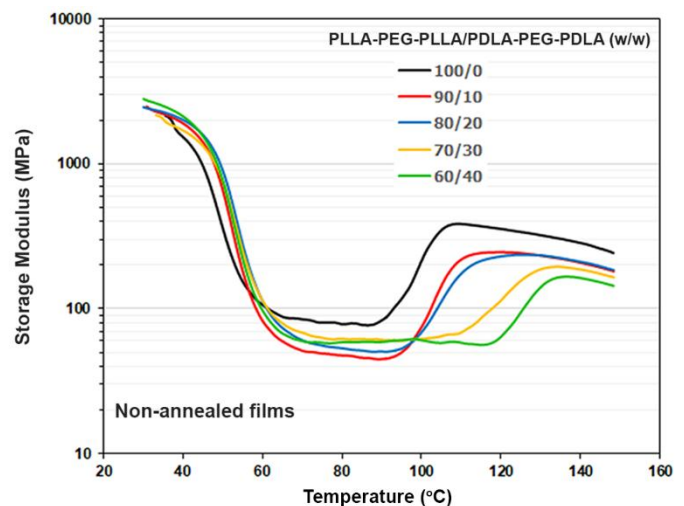


Figure 5: Storage modulus from DMA of chain-extended blend films with various PLLA-PEG-PLLA/PDLA-PEG-PDLA weight ratios.

The dimensional stability to heat of blend films was used to confirm its heat resistance. Figure 6 shows film sample before and after testing. The PLLA-PEG-PLLA/PDLA-PEG-PDLA blending reduced film extension indicates the heat resistance of films was improved. From Figure 7, the dimensional stability to heat of the films significantly increased as the PLLA-PEG-PLLA/PDLA-PEG-PDLA ratio increased. The results confirmed that the stereocomplexation of PLLA and PDLA end-blocks improved the heat resistance of the blend films. It should be noted that the chain-extended blend films exhibited higher dimensional stability to heat than the non-chain-extended blend films for the same blend ratio [18].

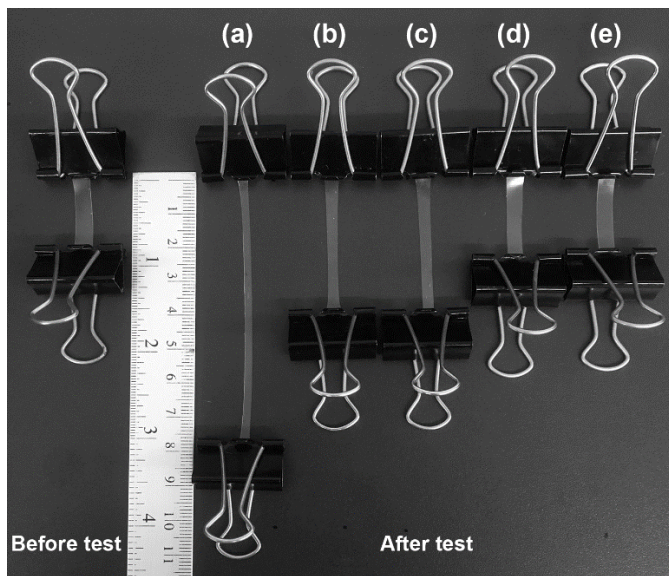


Figure 6: Photographs of chain-extended blend films with various PLLA-PEG-PLLA/PDLA-PEG-PDLA weight ratios before and after test of dimensional stability to heat.

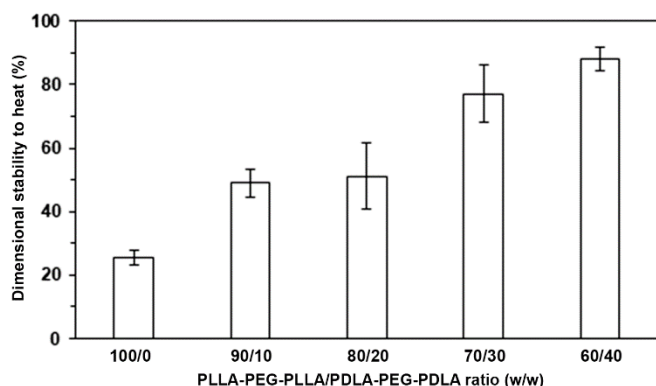


Figure 7: Dimensional stability to heat of chain-extended blend films with various PLLA-PEG-PLLA/PDLA-PEG-PDLA weight ratios.

IV. CONCLUSIONS

In summary, the chain-extended PLLA-PEG-PLLA/PDLA-PEG-PDLA blends were prepared by melt blending. The hc-

ΔH_m of the blends decreased and the sc- ΔH_m increased as the PLLA-PEG-PDLA ratio increased. From XRD, the blend films exhibited only stereocomplex crystallites. The PLLA-PEG-PDLA blending decreased the strain at break of the blend films. The heat resistance of blend films was studied using DMA method and dimensional stability to heat and found to be improved by the PLLA-PEG-PDLA blending. It can be concluded that chain extension of PLLA-PEG-PLLA/PDLA-PEG-PDLA blends decreased the extensibility but improved their heat resistance. These chain-extended blends prepared from melt process could use as flexible and highly heat-resistant bioplastic products.

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