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## Research Article

# Preparation of Biodegradable Stereocomplex Polylactide Films by Compression Molding Using Poly( $\epsilon$ -caprolactone-co-L-lactide) Copolyester as a Film Former

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## Abstract

**Background and Objective:** Bio-renewable and biodegradable stereo complex polylactides (scPLs) have widely investigated for use as high-performance bioplastic products. However, melt process ability and brittleness of the scPL were limited for this purpose. In this study, physicochemical and mechanical properties of scPL/poly( $\epsilon$ -caprolactone-co-L-lactide) copolyester blends with and without chain extension were determined. **Materials and Methods:** The scPL/copolyester blend pellets were prepared by *in situ* melt blending of poly(L-lactide), poly(D-lactide) and copolyester. The influences of the copolyester ratios (100/0, 90/10, 80/20 and 60/40 w/w) and chain extension on the characteristics of the scPL pellets, including stereo complex formation, thermal stability, melt flow index (MFI) and their film forming were determined. Properties of the compressed blend films were also investigated. **Results:** The copolyester blending enhanced the stereo complexation of the blend pellets. The MFI of the blend pellets increased with the copolyester ratio. The continuous and smooth blend films were successfully prepared using a compression molding technique when the copolyester ratio was increased up to 20% wt. The compression force also enhanced the stereo complexation of the blend films. The chain extension improved the phase compatibility of the scPL/copolyester blend films. The flexibility of the blend films slightly improved as the copolyester ratio increased. **Conclusion:** This study could provide a new insight into the synergistic effects of copolyester blending, chain extension and compression force for designing high-performance scPL products with controllable film forming and flexibility.

**Key words:** Biodegradable, stereo complex polylactide, copolyester, polymer blends, compression molding

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**Competing Interest:** The authors have declared that no competing interest exists.

**Data Availability:** All relevant data are within the paper and its supporting information files.

## INTRODUCTION

Bio-renewable and biodegradable polymers have extensively investigated for use as sustainable plastic products to reduce pollution of non-biodegradable plastic waste<sup>1,2</sup>. Poly(lactic acid) (PLA) or polylactide (PL) are bio-renewable and biodegradable polyesters that have widely studied because of its good processability and mechanical properties. Stereo complex polylactide (scPL) prepared from the blending of poly(L-lactide) (PLL) and poly(D-lactide) (PDL) has gathered much attention because it exhibits better thermal stability, mechanical strength and hydrolysis resistance than just PLL<sup>3-5</sup>. The stereo complex crystallites of the scPLs formed from the co-crystallization of the PLL/PDL blends are different from the homo-crystallites of the PLL and the PDL. The melting temperature ( $T_m$ ) of the scPL ( $T_m \gg 230^\circ\text{C}$ ) and its crystallization rate are higher than the PLL and PDL, due to the stronger Van der Waals forces in the stereo complex crystallites<sup>6-8</sup>. However, precise changes in the scPL properties by polymer blending and/or additive compounding are still required for various melt processes and applications<sup>9</sup>.

Many researchers have prepared scPL films by solution blending before film casting<sup>9</sup>. However, scPL specimens prepared by melt processing methods have been scarcely published<sup>10</sup>. The melt processing methods are suitable for larger-scale scPL production. Then scPL pellets with controllable properties are required for this purpose. Moreover, the flexibility of the scPL product is also an important factor to be considered.

Poly( $\epsilon$ -caprolactone-co-L-lactide) [P(CL-co-LL)] copolyesters show low stiffness and higher flexibility compared to PLL because they have lower glass transition temperatures<sup>11,12</sup>. These rubbery copolyesters have been used to improve the flexibility of the PLL by block copolymerization<sup>13</sup>. Copolyesters with a 50/50 (mol/mol) CL/LL ratio are not completely amorphous. The small melting peaks of the CL and LL segments of the rubbery P(CL-co-LL) copolyesters were still detected<sup>12,13</sup>. This may cause reduced flexibility in the P(CL-co-LL) copolyesters. The P(CL-co-LL) copolyesters that contain higher CL mole ratios exhibited a larger amorphous character that can improve the flexibility of the PLL better than the 50/50 P(CL-co-LL) copolyesters<sup>14</sup>.

In this study, novel scPL/copolyester blend films with and without chain extension were prepared by melt blending followed by compression molding. The copolyester was synthesized by the ring-opening polymerization of the 60/40 by mol CL/LL monomer mixture. The influences of the

copolyester ratio and chain extension on the properties of the blend pellets and blend films were determined. To the best of knowledge, this study was the first to demonstrate the improvement of the scPL melt process ability by rubbery copolyester blending. More interestingly, the synergistic effects of copolyester blending, chain extension and compression molding in the stereo complexation of compressed scPL films were evaluate for the first time.

## MATERIALS AND METHODS

This study was carried out from January, 2016 to January, 2017 at biodegradable Polymers Research Unit, Faculty of Science, Maharakham University, Thailand.

**Materials:** The L-lactide (LL) and D-lactide (DL) monomers were prepared using polycondensation followed by thermal decomposition from L-lactic acid (88%, Purac, Thailand) and D-lactic acid (90%, Haihang Industry Co., Ltd., China), respectively. The lactide monomers were purified by re-crystallization four times from ethyl acetate before drying in a vacuum oven at  $55^\circ\text{C}$  for 48 h. The  $\epsilon$ -caprolactone (CL) monomer (99%, Acros Organics, USA) and 1-Dodecanol (98%, Fluka, Switzerland) were purified by distillation under reduced pressure before use. Stannous octoate ( $\text{Sn}(\text{Oct})_2$ , 95%, Sigma, USA) was used without further purification. All reagents used were analytical grade. A styrene-acrylic multi-functional-epoxide oligomeric agent (Joncryl® ADR 4368) in flake form with a molecular weight of  $6,800 \text{ g mol}^{-1}$  (an epoxy equivalent weight of  $285 \text{ g mol}^{-1}$ ) was used as a chain extender and it was supplied by BASF, Thailand.

**Synthesis of poly lactides:** The poly(L-lactide) (PLL) and poly(D-lactide) (PDL) were synthesized by ring-opening polymerization in bulk from the LL and DL monomers, respectively, at  $165^\circ\text{C}$  for 2.5 h under a nitrogen atmosphere using stannous octoate (0.01 mol %) and 1-Dodecanol (0.14 mol %) as the initiating system, as previously reported in this study<sup>15</sup>. The obtained poly lactides (PL) were granulated before drying in a vacuum oven at  $110^\circ\text{C}$  for 3 h to remove the un-reacted lactide. The resulting PLL and PDL with  $M_n$  values of approximately  $90,000 \text{ g mol}^{-1}$  were obtained from the GPC. The L- and D-enantiomer contents obtained from the polarimetry were 96 and 97% for the PLL and the PDL, respectively.

**Synthesis of copolyester:** The poly( $\epsilon$ -caprolactone-co-L-lactide) copolyester with CL/LL ratio of 60/40 by mole was

synthesized by ring-opening polymerization in bulk at 145°C for 12 h under a nitrogen atmosphere using 0.02 mol% stannous octoate and 0.12 mol% 1-Dodecanol as the initiating system. The resulting copolyester was cut into small pieces before drying in a vacuum oven at 110°C for 3 h to remove the un-reacted monomers. The  $M_n$  and MWD values of the copolyester obtained from the GPC were 85,000 g mol<sup>-1</sup> and 2.1, respectively. The CL/LL ratio and glass transition temperature ( $T_g$ ) of the copolyester obtained from the H-NMR and DSC methods were 58/42 by mole and -24°C, respectively. The copolyester was completely amorphous.

**Preparation of scPL/copolyester blend pellets and blend films:** The PLL, PDL, copolyester and Joncryl® ADR4368 (chain extender) were dried in a vacuum oven at 50°C overnight before melt blending. The PLL, PDL, copolyester and 1.0 phr Joncryl® ADR4368 were *in situ* melt blended to prepare chain extended scPL/copolyester blends using an internal mixer (HAAKE PolyLab OS system) at 200°C for 4 min. A rotor speed of 100 rpm was chosen. The PLL/PDL ratio was kept constant at 50/50 (w/w). The scPL/copolyester ratios of 100/0, 90/10, 80/20 and 60/40 (w/w) were investigated. The non-chain extended 80/20 (w/w) scPL/copolyester blend was also prepared by the same method for comparison. The obtained scPL/copolyester blends were granulated to obtain blend pellets and dried in a vacuum oven at 50°C overnight before characterization and film forming.

The scPL/copolyester blend films were prepared from the blend pellets by an Auto CH CARVER® compression molding machine at 240°C for 5 min with a compression force of 10 t. The film thicknesses were approximately 150-250 μm. The blend films were kept at room temperature for 24 h before characterization.

**Characterization of scPL/copolyester blend pellets and blend films:** The thermal transition properties of the scPL/copolyester blend pellets and blend films were determined with a Perkin-Elmer Pyris Diamond differential scanning calorimeter (DSC) under a nitrogen flow. For DSC, 3-5 mg of each sample were heated at 10°C min<sup>-1</sup> over a temperature range of -40-250°C (1st heating scan). Then, the samples were quenched to -40°C according to the DSC instrument's own default cooling mode before heating from -40-250°C (2nd heating scan). The degree of homo-crystallinity ( $X_{hc}$ ) and stereo complex crystallinity ( $X_{sc}$ ) of the blend pellets and films were calculated from the enthalpies of melting of the homo-crystallites ( $\Delta H_{hc}$ ) and stereo complex crystallites ( $\Delta H_{sc}$ ) using Eq. 1, 2, respectively:

$$X_{hc} = [\Delta H_{hc}/(93.7 \text{ J/g } f_{scPL})] \times 100\% \quad (1)$$

$$X_{sc} = [\Delta H_{sc}/(142 \text{ J/g } f_{scPL})] \times 100\% \quad (2)$$

where,  $\Delta H_{hc}$  and  $\Delta H_{sc}$  were the enthalpies of melting of the homo-crystallites and stereocomplex crystallites, respectively, that were obtained from the DSC curves. The  $f_{scPL}$  is the weight fraction of the scPL in the blend samples. The enthalpies of melting for 100% crystallinity of the homo-crystallite and stereocomplex crystallite were 93.7 and 142 J g<sup>-1</sup>, respectively<sup>15</sup>.

The thermal stability of the blend pellets was determined with a TA-Instrument SDT Q600 thermogravimetric analyzer (TGA) in a non-isothermal mode. For TGA analysis, samples of 5-10 mg were heated at 20°C/min under a nitrogen atmosphere over the temperature range 50-800°C to assess the temperature of the maximum decomposition rate ( $T_{d,max}$ ). The melt flow index (MFI) of the blend pellets was measured using a Tinius Olsen MP1200 melt flow indexer. The temperature of the melt was kept at a uniform 235°C and a 5.0 kg load was applied to extrude the molten blends<sup>15</sup>. A 100 g rod was used as a plunger. The MFI was averaged from at least five determinations.

The morphology of the blend film fractures was determined by scanning electron microscopy (SEM) using a JEOL JSM-6460LV SEM. The blend films were immersed in liquid nitrogen for 20 min before film fracture. The film samples were coated with gold to enhance conductivity before scanning.

The wide angle X-ray diffraction (WAXD) patterns of the blend films were recorded with a Bruker D8 Advance wide-angle X-ray diffractometer at 25°C using CuKα radiation at 40 kV and 40 mA. For WAXD, the scanning angle range of  $2\theta = 5-30^\circ$  at a scan speed of 3° min<sup>-1</sup> was used to investigate the homo-crystalline and stereocomplex crystalline structures of the blend films.

The tensile properties, including stress at break, elongation at break and initial Young's modulus, of the blend films were determined at 25°C and 65% relative humidity with a Lloyds LRX+ Universal Mechanical Testing Machine. The film samples (80' 10 mm) were tested with a gauge length of 25 mm and a crosshead speed of 10 mm min<sup>-1</sup>. The tensile properties were averaged from 5 measurements for each sample.

## RESULTS

**Characterization of scPL/copolyester blend pellets:** The commercial PLL and PDL products have usually reacted with

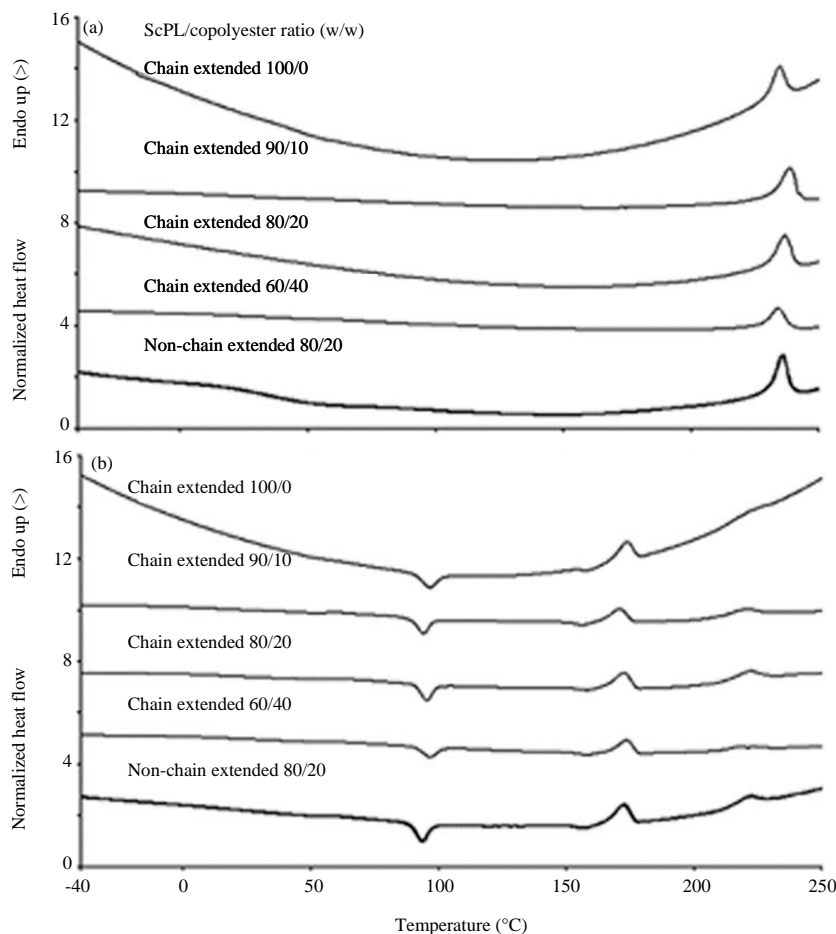


Fig. 1(a-b): (a) First heating scan DSC thermograms of chain extended and non-chain extended scPL/copolyester blend pellets and (b) second heating scan DSC thermograms of chain extended and non-chain extended scPL/copolyester blend pellets

chain extender to adjust its melt strength for each melt process technique. In this study, both the chain extender-free PLL and PDL were then synthesized for clear investigation the influence of the chain extender on blend properties. The PLL, PDL and P(CL-co-LL) copolyester synthesized by the ring-opening polymerization reactions were *in situ* melt blended at 200°C for 4 min using a PLL/PDL ratio of 50/50 (w/w) and scPL/copolyester [(PLL+PDL)/copolyester] ratios of 100/0, 90/10, 80/20 and 60/40 (w/w) to prepare the scPL/copolyester blend pellets. The PLL and PDL were semi-crystalline state. Meanwhile the copolyester was a rubbery amorphous state.

**Thermal transition properties:** The thermal transition properties of the neat scPL and blend pellets with and without chain extension were determined from the DSC thermograms, as shown in Fig. 1. All the 1st heating scan DSC thermograms in (Fig. 1a) showed only a single melting temperature of

stereocomplex crystallites ( $T_{m,sc}$ ) which were similar to the range 234-239°C. The copolyester blending and chain extension did not significantly affect the  $T_{m,sc}$  of the blend pellets. The stereocomplex crystallinities ( $X_{sc}$ ) of the scPL were calculated from the enthalpy of melting of the stereocomplex crystallites ( $\Delta H_{m,sc}$ ) using Eq. 2. The DSC results of the blend pellets from the 1st heating scan are summarized in Table 1.

The  $X_{sc}$  values of the blend pellets with and without chain extension (46.5-57.4%) were higher than that of the neat scPL pellets (36.9%). The 80/20 (w/w) scPL/copolyester ratio showed the highest  $X_{sc}$  (53.8%) for the chain extended blend pellets. However the  $X_{sc}$  decreased to 46.5% when the copolyester ratio increased from 20-40% wt. The  $X_{sc}$  of the non-chain extended blend pellets (57.4%) was slightly higher than the chain extended blend pellets (53.8%) for the 80/20 (w/w) blend ratio.

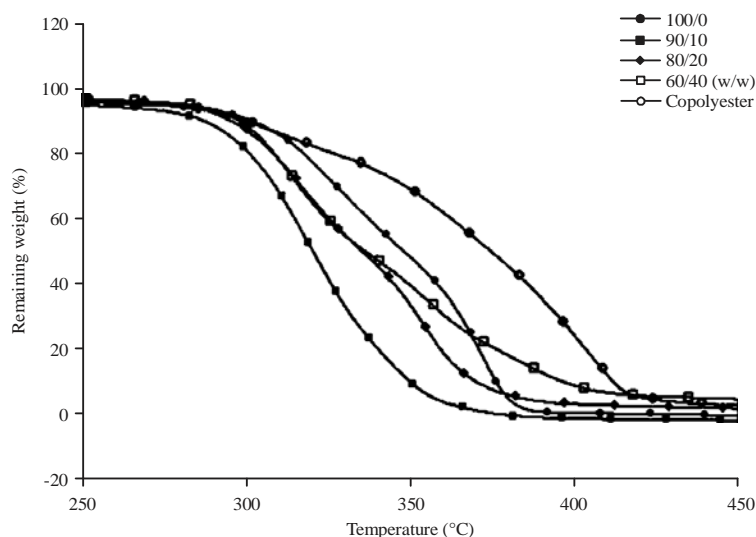


Fig. 2: TG thermograms of chain extended blend pellets prepared with different scPL/copolyester ratios

Table 1: Thermal transition properties of neat scPL and blend pellets from 1st heating scan DSC thermograms

scPL/copolyester ratio (w/w)	Joncryl <sup>®</sup> (phr)	$T_{m,sc}$ (°C)	Dhsc (J g <sup>-1</sup> )	$X_{sc}$ (%)
100/0	1	235	52.4	36.9
90/10	1	239	65.3	51.1
80/20	1	237	61.1	53.8
60/40	1	234	39.6	46.5
80/20	-	236	65.2	57.4

$T_{m,sc}$ : Melting temperature of stereocomplex crystallites, Dhsc: Enthalpy of melting of stereocomplex crystallites,  $X_{sc}$ : Degree of stereocomplex crystallinity

Table 2: Thermal transition properties of neat scPL and blend pellets from 2nd heating scan DSC thermograms

scPL/copolyester ratio (w/w)	Joncryl <sup>®</sup> (phr)	$T_{g1}$ (°C)	$T_{g2}$ (°C)	$T_c$ (°C)	$\Delta H_c$ (J g <sup>-1</sup> )	$T_{m,hc}$ (°C)	$T_{m,sc}$ (°C)	$\Delta H_{hc}$ (J g <sup>-1</sup> )	$\Delta H_{sc}$ (J g <sup>-1</sup> )
100/0	1	-	58	97	23.2	174	222	31.0	9.6
90/10	1	-22	55	94	21.5	171	220	25.4	27.1
80/20	1	-24	56	96	20.7	173	222	24.7	30.3
60/40	1	-24	57	97	15.5	174	219	21.0	10.2
80/20	-	-18	56	94	22.8	172	222	31.2	18.6

$T_{g1}$ : Glass transition temperature of copolyester component,  $T_{g2}$ : Glass transition temperature of scPL component,  $T_c$ : Crystallization temperature,  $\Delta H_c$ : Enthalpy of crystallization,  $T_{m,hc}$ : Melting temperature of homo-crystallites,  $T_{m,sc}$ : Melting temperature of stereocomplex crystallites,  $\Delta H_{hc}$ : Enthalpy of melting of homo-crystallites,  $\Delta H_{sc}$ : Enthalpy of melting of stereocomplex crystallites

The 2nd heating scan DSC thermograms in Fig. 1b showed the glass transition temperature ( $T_g$ ), crystallization temperature ( $T_c$ ), melting temperature of homo-crystallites ( $T_{m,hc}$ ) and  $T_{m,sc}$  of the blend pellets as reported in Table 2. The  $T_c$ ,  $T_{m,hc}$  and  $T_{m,sc}$  values of the blend pellets were similar in the ranges 94-97°C, 171-174°C and 219-222°C, respectively. The  $\Delta H_c$  and  $\Delta H_{m,hc}$  of the chain extended blend pellets slightly decreased as the copolyester ratio increased. However, the  $\Delta H_{m,sc}$  values of all the blend pellets were higher than the neat scPL pellets (9.6 J g<sup>-1</sup>).

From the expanded 2nd heating scan DSC curves, the neat scPL pellets exhibited a single  $T_g$  at 58°C. The blend pellets showed both the  $T_g$  of the copolyester ( $T_{g1}$ ) and scPL ( $T_{g2}$ ) components in the ranges -24 to -22°C and 55-57°C, respectively. These  $T_g$  values were similar to those of the  $T_g$  of the copolyester (-24°C) and scPL (58°C).

**Thermal stability:** The thermal stability of the blend pellets was investigated from TG thermograms. The neat scPL and copolyester exhibited thermal decomposition in the ranges 250-400 and 250-450°C, respectively, as shown in Fig. 2. The chain extended blend pellets exhibited lower thermal stability than the neat scPL. However, the thermal stabilities of the blend pellets slightly increased as the copolyester ratio increased. From Fig. 3, it can be seen that the thermal stability of the chain extended scPL blend pellets in range 300-350°C was lower than that of the non-chain extended pellets for the 80/20 (w/w) blend pellets. The copolyester blending and chain extension reduced thermal stability of the blend pellets.

More data on the thermal stability of the blend pellets were determined from derivative TG (DTG) thermograms, as shown in Fig. 4. The peaks of temperature of maximum decomposition rate ( $T_{d,max}$ ) of the samples were detected. The

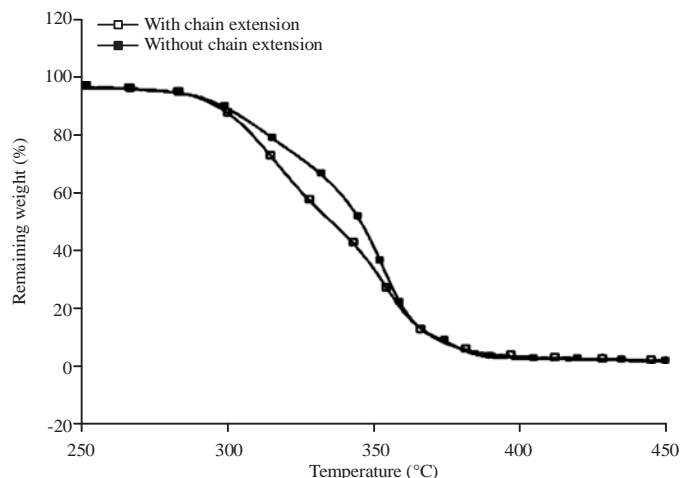


Fig. 3: TG thermograms of 80/20 (w/w) scPL/copolyester blend pellets

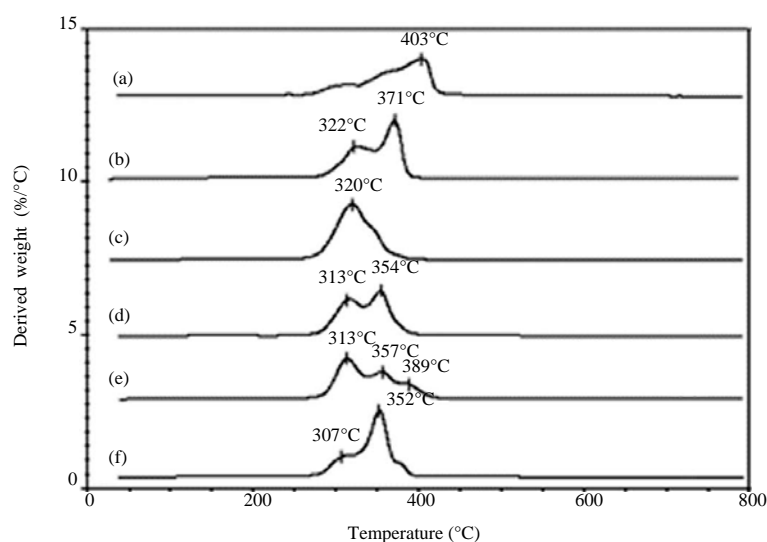


Fig. 4(a-f): DTG thermograms of (a) Copolyester and chain extended blend pellets prepared with scPL/copolyester ratios of (b) 100/0, (c) 90/10, (d) 80/20 and (e) 60/40 (w/w) as well as and (f) Non-chain extended 80/20 (w/w) scPL/copolyester blend pellets

copolyester had a single  $T_{d,max}$  at 403°C (Fig. 4a), while the neat scPL pellets had two  $T_{d,max}$  at 322°C and 371°C (Fig. 4b). The chain extended 90/10 (w/w) scPL/copolyester blend pellets showed a single  $T_{d,max}$  at 320°C (Fig. 4c). When the copolyester blend ratio increased up to 20 and 40%, the other  $T_{d,max}$  peaks of the copolyester component were observed (Fig. 4d, e). The non-chain extended 80/20 (w/w) scPL/copolyester blend pellets in Fig. 4f showed the main  $T_{d,max}$  peak at 352°C and the small  $T_{d,max}$  peak at 307°C. The DTG profiles of the chain extended and non-chain extended scPL/copolyester blend pellets in (Fig. 4d, f, respectively), were different. This confirms the effect of chain extension on thermal stability of the blend pellets.

Table 3: Melt flow index of neat scPL and blend pellets (235°C-5.0 kg)

scPL/copolyester ratio (w/w)	Joncryl® (phr)	MFI (g/10 min)
100/0	1	30±0.6
90/10	1	48±7.8
80/20	1	54±4.8
60/40	1	72±13.8
80/20	-	ND

ND: Not determined

**Melt flow index:** The resulting MFI values are summarized in Table 3. The MFI of the copolyester was not measured because the copolyester was too liquid at 235°C, which suggests its melt strength was too low. The MFI of the chain extended blend pellets strongly depended upon the copolyester

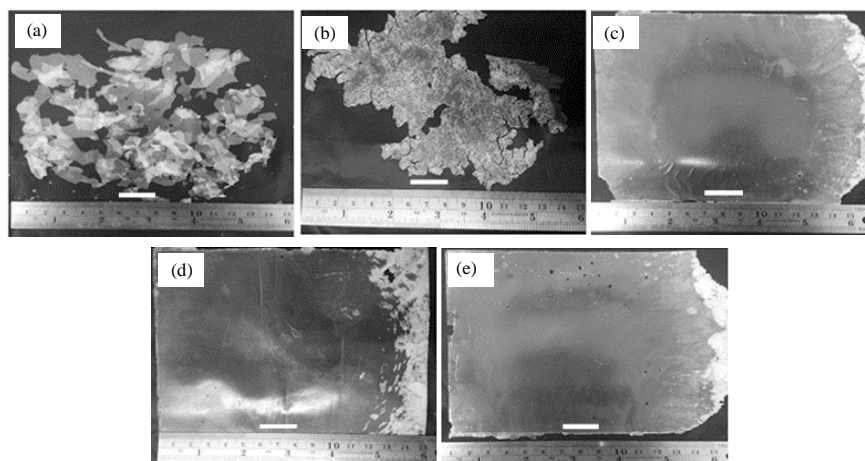


Fig. 5(a-e): Pictures of chain extended blend films prepared by compression molding with scPL/copolyester ratios of (a) 100/0, (b) 90/10, (c) 80/20 and (d) 60/40 (w/w) as well as and (e) Non-chain extended 80/20 (w/w) scPL/copolyester blend film (all bar scales = 2 cm)

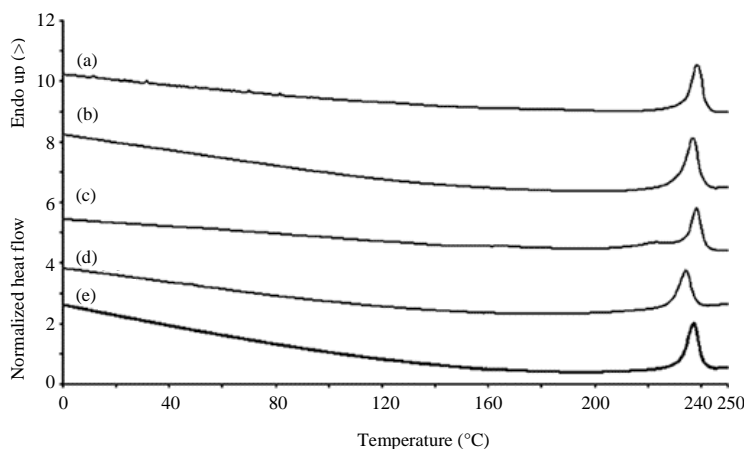


Fig. 6(a-e): First heating scan DSC thermograms of chain extended blend films prepared with scPL/copolyester ratios of (a) 100/0, (b) 90/10, (c) 80/20 and (d) 60/40 (w/w) as well as and (e) Non-chain extended 80/20 (w/w) scPL/copolyester blend film

ratio. The MFI of the chain extended blend pellets increased steadily (melt strength decreased) as the copolyester ratio increased. In addition, the melt strength of the non-chain extended 80/20 (w/w) scPL/copolyester blend pellets was also too low, so its MFI was not measured.

**Characterization of scPL/copolyester blend films:** The blend films were prepared by compression molding of the blend pellets at 240°C with a 10 t load. The resulting blend films are presented in Fig. 5. It can be seen that the neat scPL film (Fig. 5a) was very brittle after cooling. The continuous scPL film was not obtain, which may be due to it being very brittle. A small amount of the continuous scPL film

was formed when the 10% wt. copolyester was blended (Fig. 5b). However, it was still very brittle. The chain extended blend films with continuous and smooth surfaces were obtained when the copolyester ratios were increased up to 20 and 40% wt., as shown in (Fig. 5c, d), respectively. The blend film of the non-chain extended 80/20 (w/w) scPL/copolyester was also continuous, as shown in Fig. 5e. Their film thicknesses were in range 150-250 mm. The results suggested that the copolyester can act as a film former to improve the film forming property of the scPL.

**Thermal transition properties:** Figure 6 shows the 1st heating scan DSC thermograms of the film samples. It



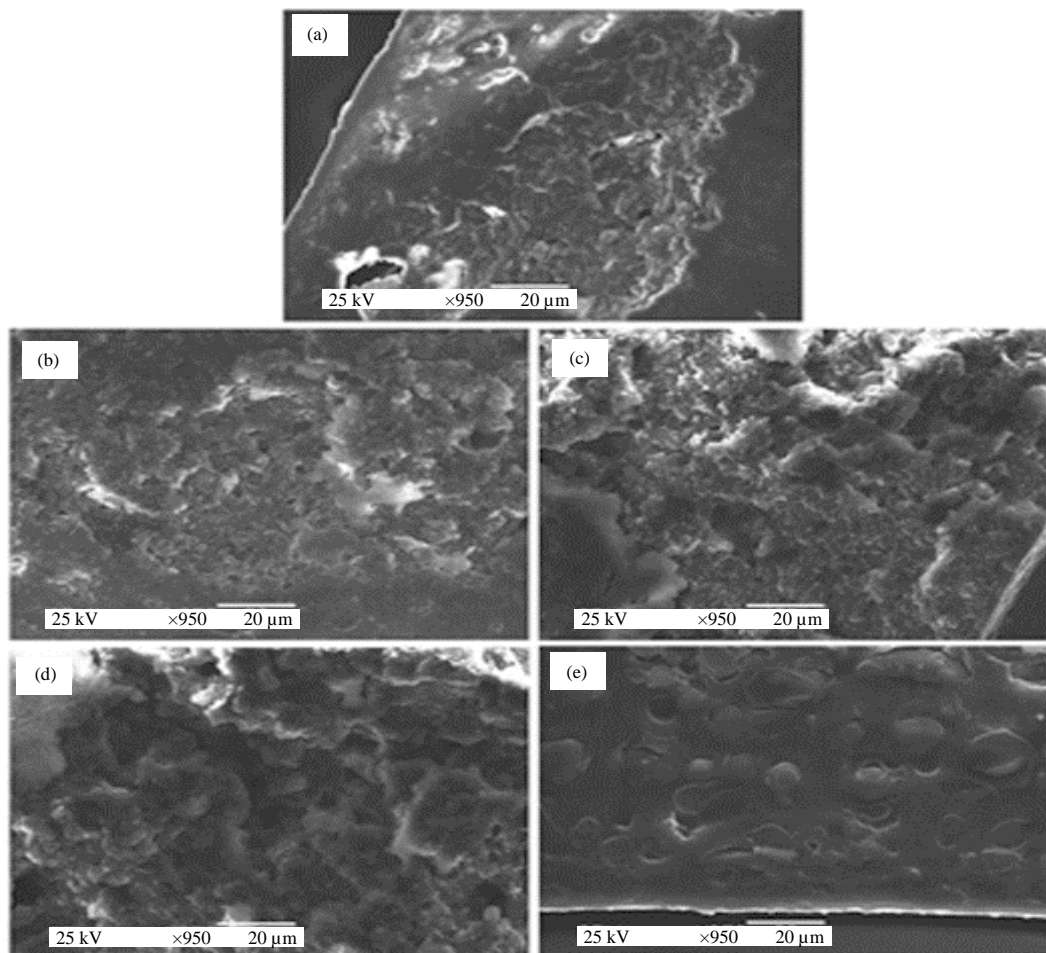


Fig. 7(a-e): SEM images of cross-sections of chain extended blend films prepared with scPL/copolyester ratios of (a) 100/0, (b) 90/10, (c) 80/20 and (d) 60/40 (w/w) as well as and (e) Non-chain extended 80/20 (w/w) scPL/copolyester blend film (all bar scales = 20  $\mu\text{m}$ )

Table 4: Thermal transition properties of neat scPL and blend films from 1st heating scan DSC thermograms

scPL/copolyester ratio (w/w)	Joncryl® (phr)	$T_{m,sc}$ ( $^{\circ}\text{C}$ )	$\Delta H_{sc}$ ( $\text{J g}^{-1}$ )	$X_{sc}$ (%)
100/0	1	238	58.4	41.1
90/10	1	237	71.7	56.1
80/20	1	238	63.2	55.6
60/40	1	234	43.6	51.2
80/20	-	237	54.1	47.6

$T_{m,sc}$ : Melting temperature of stereocomplex crystallites,  $\Delta H_{sc}$ : Enthalpy of melting of stereocomplex crystallites,  $X_{sc}$ : Degree of stereocomplex crystallinity

is surprising that only single  $T_{m,sc}$  peaks were detected for the neat scPL and all blend films. This indicates that the compression force also enhanced the stereocomplexation of the blend films during film formation. The 2nd heating scan DSC thermograms of the film samples (DSC curves not shown) exhibited both  $T_{m,hc}$  and  $T_{m,sc}$  similar to the 2nd heating scan DSC thermograms of the blend pellets in Fig. 1b.

The DSC results of the film samples are summarized in Table 4. The  $T_{m,sc}$  of the blend films were similar in the range

234-238 $^{\circ}\text{C}$ . The  $X_{sc}$  values of all the blend films (47.6-56.1%) were higher than that of the neat scPL film (41.1%), which corresponds to the results of the blend pellets.

**Phase morphology:** The phase morphology of the film samples was determined from SEM images of the film cross-sections, as shown in Fig. 7. The roughness of the film cross-sections increased as the copolyester was blended and the copolyester ratios were increased

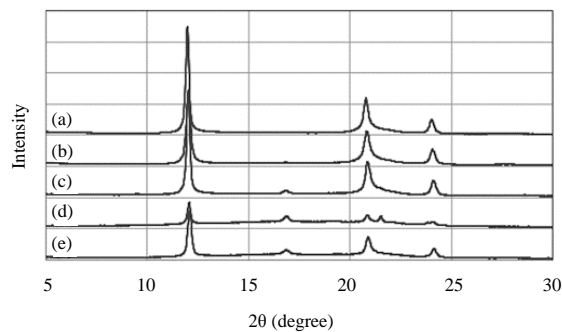


Fig. 8(a-e): WAXD patterns of chain extended blend films prepared with scPL/copolyester ratios of (a) 100/0, (b) 90/10, (c) 80/20 and (d) 60/40 (w/w) as well as and (e) Non-chain extended 80/20 (w/w) scPL/copolyester blend film

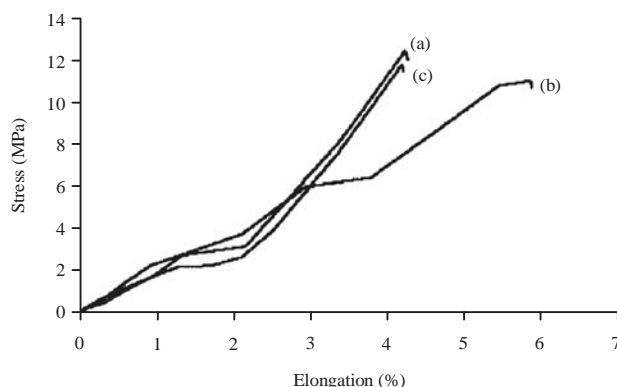


Fig. 9(a-c): Tensile profiles of chain extended blend films prepared with scPL/copolyester ratios of (a) 80/20 and (b) 60/40 (w/w) as well as and (c) Non-chain extended 80/20 (w/w) scPL/copolyester blend film

(Fig. 7b-d). The sticky copolyester phases with irregular shape in the film matrices were observed for all the chain extended blend films. The aggregate sizes of the sticky copolyester phases increased as the copolyester ratio increased.

Moreover, the non-chain extended blend film in Fig. 7e clearly exhibited phase separation of the continuous scPL and dispersed copolyester phases. The dispersed copolyester phases were nearly spherical shape and 5-20 nm in size. In addition, gaps between the two phases were also observed.

**Crystalline structures:** The crystalline structures of the film samples were determined from the WAXD patterns, as illustrated in Fig. 8. Only the diffraction peaks at  $2\theta$  of 12, 21 and  $24^\circ$  were observed for the neat scPL film (Fig. 8a) that can be ascribed to the stereocomplex crystallites<sup>8,16</sup>. The diffraction peak at  $2\theta$  of  $17^\circ$ , corresponding to the homo-crystallites<sup>8,16</sup> was not detected. The weak diffraction peaks at  $2\theta$  of  $17^\circ$  of the homo-crystallites were observed when the copolyester was blended Fig. 8b,d. The peak intensities of homo-crystallites increased with the copolyester ratio. However, the stereocomplex crystallites were predominantly formed for all

the blend films. The non-chain extended blend film in Fig. 8e showed a WAXD pattern similar to the chain extended blend film in Fig. 8c for the 80/20 (w/w) blend films.

**Tensile properties:** The tensile properties of the blend films were investigated from the tensile curves as shown in Fig. 9. The chain extended neat scPL and 90/10 (w/w) blend films were not tested as they were brittle films Fig. 5a-b. It can be seen that the stress at break of the chain extended blend films slightly decreased and the elongation at break slightly increased as the copolyester ratio was increased from 20-40% wt. The tensile results are summarized in Table 5. The initial Young's modulus decreased and the elongation at break increased as the copolyester blend ratio increased. The tensile properties of the non-chain extended 80/20 (w/w) blend film were slightly lower than the chain extended blend film.

## DISCUSSION

The PLL/PDL ratio was fixed at 50/50 (w/w) because this is the most favorable ratio for stereocomplex formation<sup>17,18</sup>.

Table 5: Tensile properties of neat scPL and blend films

scPL/copolyester ratio (w/w)	Joncryl® (phr)	Initial Young's modulus (MPa)	Stress at break (MPa)	Elongation at break (%)
100/0	1	- <sup>a</sup>	- <sup>a</sup>	- <sup>a</sup>
90/10	1	- <sup>a</sup>	- <sup>a</sup>	- <sup>a</sup>
80/20	1	500.1 ± 63.9	12.7 ± 1.7	4.2 ± 0.4
60/40	1	276.7 ± 31.1	10.3 ± 1.5	5.9 ± 0.9
80/20	-	436.5 ± 52.7	11.2 ± 2.1	3.7 ± 0.5

<sup>a</sup>Cannot be determined

Influences of copolyester blending and chain extension on PLL/PDL stereocomplexation were then clearly investigated on the 50/50 (w/w) ratio.

From the  $X_{sc}$  results of the blend pellets in Table 1 suggest that the copolyester blending enhanced stereocomplexation. The copolyester can act as a nucleating agent for stereocomplex crystallization of the scPL matrices. However, the higher copolyester content (40%wt.) suppressed stereocomplex crystallization. The chain extension of the scPL/copolyester blends also inhibited stereocomplexation. This may be explained by the longer PL chains of the chain extended scPL that suppressed stereocomplex formation<sup>19</sup>. The longer PL chains were obtained by chain extension. The results of 2nd heating scan DSC thermograms in Table 2 confirm that the copolyester blending suppressed homo-crystallization and enhanced stereocomplex crystallization according to the 1st heating scan DSC results. In addition, two  $T_g$  values of each blend pellets in Table 2 indicate the phase separation between the scPL and the copolyester had occurred.

From Fig. 2, the thermal stability of the copolyester was better than the neat scPL due to the higher thermal stability of the CL segments<sup>20</sup>. The lower copolyester ratio (10% wt.) decreases thermal stability of the blends. The interpenetrated copolyester chains reduced intermolecular forces in the scPL matrix. However, the higher copolyester ratios (20 and 40% wt.) improved the thermal stability. This may be due to the higher thermal stability of the copolyester fraction. The chain extension of the blends reduced its thermal stability. The branching structure of the chain-extended blend pellets could decrease intermolecular forces in the blends.

The lower  $T_{d,max}$  of the neat scPL pellets in Fig. 4b could be due to the shorter PL chain decomposition<sup>21</sup>. The lower single  $T_{d,max}$  of the chain extended 90/10 (w/w) blend pellets at 320°C could explain by the interpenetration of the copolyester chains that decreased the intermolecular forces of the scPL matrix. The higher copolyester ratios induced more phase separation. This induces various  $T_{d,max}$  peaks of each phase. The difference in the DTG profiles of the chain extended and

non-chain extended 80/20 (w/w) blend pellets suggested that the copolyester chains could also react with the chain extender molecules. This enhances phase compatibility.

Usually the Joncryl® chain extender is used to improve the melt strength (decrease melt flow index; MFI) of the PL by branching the structural formation<sup>22</sup>. In this study, the MFI of the neat scPL and blend pellets was determined at 235 °C with a 5.0 kg load according to our previous paper<sup>15</sup>. The melt strength of the blend pellets was improved by the chain extension to decrease the MFI values. This is due to the chain extension changed the molecular structures of the PL from linear to branched<sup>22</sup>. The copolyester blending decreases melt strength (increases MFI) of the blend pellets because of the melt strength of the copolyester is too low.

Usually, the homo-crystallization of the scPL occurs after the scPL is molten<sup>7,15</sup>. The single  $T_{m,sc}$  peaks of the compressed scPL and blend films suggested the compression force induced stereocomplexation in the molten scPL. Song *et al.*<sup>23</sup> has reported that a shear force accelerated the stereocomplex formation of the molten scPL<sup>23</sup>. While both  $T_{m,hc}$  and  $T_{m,sc}$  peaks of were detected for the 2nd heating scan DSC thermograms of the blend films. This can be explained due to there being no compression force on the DSC crucible during the melting stage. This is important data on stereocomplex formation of the scPL under a molten state. The copolyester blending also enhanced the  $X_{sc}$  values of the blend films. Therefore, compression force and copolyester blending are synergic effects for stereocomplexation of the compressed scPL films.

The roughness of the neat scPL film cross-sections in Fig. 7a consisted of a large number of small particles due to the formation of small crystallites<sup>4,24</sup>. The faster crystallization of the scPL could induce the small crystallites<sup>24</sup>. The higher copolyester ratios induced larger aggregated copolyester phases due to the rubber-like property of the copolyester.

The non-chain extended 80/20 (w/w) blend film contained de-bonded copolyester particles throughout the film cross-section suggested low phase compatibility had occurred<sup>25</sup>. The phase morphology results suggest that the

chain extension improved the phase compatibility in the scPL/copolyester blends. The Joncryl® chain extender reacted with both the -COOH and -OH end groups of the polyesters<sup>26</sup>. The chain extender has been used as a reactive compatibilizer of the PL/polyester blends<sup>27,28</sup>. Therefore, both the PL and P(CL-co-LL) copolyesters can react with the Joncryl® ADR 4368 to form a reactive compatibilizer for scPL/copolyester blends according to the DTG results as described above.

The WAXD results of blend films supported that the copolyester blending with the 10 and 20% wt. enhanced stereocomplexation according to the DSC results. The weak diffraction peak at  $2\theta$  of  $22^\circ$  was also observed for the 40% copolyester (Fig. 8d) that can be ascribed to the crystallites of the PCL segments<sup>29</sup>. It can be concluded that the copolyester blending and chain extension did not affect the crystalline structure of the scPL films.

The continuous scPL films can be prepared by melt blending with the 20% wt. or higher copolyester ratios before compression molding. The copolyester acted as a film former. The rubber-like property of copolyester induced continuous scPL films. The tensile results of the blend films suggested that the copolyester blending also improved the extension of the scPL films. This is due to rubber-like characteristic of the copolyester. The branched structures of blend films obtained from the chain extension slightly decrease the mechanical properties of the blend film.

## CONCLUSION

It is concluded that the copolyester blending with 20% wt. or higher enhanced formation of compressed scPL films. The  $X_{sc}$  of the scPL was increased by copolyester blending. The thermal stability behaviors indicated that both the PL and copolyester could be chain extended with the Joncryl®. The MFI values of the blend pellets steadily increased with the copolyester ratio and decreased with the chain extension. The compression force also enhanced the stereocomplexation of the scPL films. The chain extension and copolyester blending improved the compatibility and flexibility of the blend films, respectively. More importantly, these novel scPL/copolyester blends might be applicable for the high-performance bioplastic industry. Increases in the stereocomplex crystallinity, flexibility and melt processability of the scPL by the *in situ* copolyester blending were achieved. This study could provide a guideline for other melt processes of scPL products.

## SIGNIFICANCE STATEMENT

This study discovers the possible synergistic effect of copolyester blending, chain extension and compression force that can be beneficial for stereocomplexation and film formation of high-performance polylactide products. This study will help the researcher to uncover the critical area of melt processing of stereocomplex polylactide bioplastics that many researchers were not able to explore. Thus, a new theory on blending of poly(L-lactide), poly(D-lactide), copolyester and chain extender as well as compression force, may be arrived at.

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