Mechanical properties and heat resistance of stereocomplex polylactide/copolyester blend films prepared by \textit{in situ} melt blending followed with compression molding

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Abstract

This work focuses on the process to obtain high heat-resistant stereocomplex polylactide (scPLA)/copolyester blend films by \textit{in situ} melt blending of high molecular-weight poly(L-lactide) (PLLA), low molecular-weight poly(D-lactide) (PDLA) and copolyester followed with compression molding. A copolyester of poly(\(\varepsilon\)-caprolactone-\textit{co}-L-lactide) was used as a film former. Stereocomplexation, mechanical properties and heat resistance of the scPLA/copolyester blend films were investigated by differential scanning calorimetry (DSC), tensile testing and dynamic mechanical analysis (DMA), respectively. The PDLA fractions enhanced stereocomplexation and heat resistance of the blend films while the copolyester fraction reduced film brittleness. Dimensional stability to heat of blend films was also determined and was accorded to their DMA results. It was concluded that the high heat-resistant and less brittle scPLA films could be prepared using 70/30 (w/w) PLLA/PDLA with 20 wt% copolyester through melt blending.
blending before compression molding. This film showed similar stress at break and heat resistance to those of polypropylene film but with lower strain at break.

Keyword: Materials science

1. Introduction

Sterecomplex poly(lactic acid)s or polylactides (scPLA) are poly(L-lactide)/poly(D-lactide) (PLLA/PDLA) blends that have been widely investigated for potential use as high-performance biodegradable bioplastics instead of petroleum-based and non-biodegradable plastics. This is because the scPLA showed better mechanical properties, heat resistance and hydrolysis resistance than did PLLA [1, 2, 3, 4]. The stereocomplex crystallites of scPLA have faster crystallization and higher melting points than the homo-crystallites of PLLA, due to the stronger intermolecular interactions in the stereocomplex crystallites [5, 6, 7].

There have been many reports of scPLA films prepared by solution blending [1, 8, 9, 10, 11, 12]. However, fabrication of scPLA by melt processing is interesting because of its possible use in industrial-scale applications. In this work, scPLA films were prepared by melt blending before compression molding. To the best of our knowledge, the scPLA films prepared from compression molding have been reported infrequently [13, 14]. In our previous work, continuous and less brittle scPLA films were successfully fabricated by in situ melt blending of 50/50 (w/w) PLLA/PDLA mixture with a rubber-like copolyester of 60/40 mol% poly(ε-caprolactone-co-L-lactide) [P(CL-co-LLA)] before compression molding [14]. This high molecular-weight (M.W.) P(CL-co-LLA) acted as a film former.

It has been reported that the M.W. of both PLLA and PDLA significantly affected their stereocomplexation [15]. The low M.W. PLAs have been shown to be more efficient for stereocomplexation in crystalline phase due to their good chain-diffusion [16, 17]. The higher melting temperature and faster crystallization of stereocomplex crystallites of PLA had enhanced heat-resistant property compared with the homo-crystallites. The scPLA showed better mechanical properties than the PLLA because of a high density of tie chains between the stereocomplex crystallites. The longer PLLA and PDLA chains in scPLA matrix could improve mechanical properties by linking among stereocomplex crystallites which acted as physical cross-linkers [16, 17, 18]. However, stereocomplexation, mechanical properties and heat resistance of scPLA films prepared from melt process needs to be better understood for use in practical applications. The high heat-resistance of scPLA films is required for specific applications such as heat-treatment food packaging, hot fill packaging and microwave applications.
This work sought to improve heat resistance of high M.W. PLLA by stereocomplex formation with low M.W. PDLA and also employed the copolyester to reduce the brittleness of scPLA films. The purpose of this work was therefore to investigate the influences of PLLA/PDLA ratios and copolyester contents on stereocomplexation, mechanical properties and heat resistance of scPLA films. The blend films were prepared by in situ melt blending before compression molding. Moreover, testing of dimensional stability to heat of the film samples was performed to confirm the results of heat resistance. The results were also compared with high heat-resistant polypropylene film.

2. Experimental

2.1. Materials

L-lactide (LLA) and D-lactide (DLA) monomers were synthesized from L-lactic acid (optical purity > 95%, Purac, Thailand) and D-lactic acid (optical purity > 99%, Haihang Industry Co. Ltd., China), respectively, using a polycondensation followed with a thermal depolymerization. Both lactide monomers were separately purified by re-crystallization from ethyl acetate four times before drying in a vacuum oven at 50 °C for 24 h. e-Caprolactone monomer (CL, 99% Acros organics, USA) and 1-Dodecanol initiator (98%, Fluka, Switzerland) were purified by distillation under reduced pressure before use. Stannous octoate (Sn(Oct)₂, 95%, Sigma, USA) was used without further purification. All reagents used were analytical grade. Polypropylene was purchased from IRPC, Thailand with melt flow index of 13.75 g/10 min at 210 °C for 2.16 kg load.

2.2. Synthesis of PLLA, PDLA and copolyester

High M.W. PLLA and low M.W. PDLA with feed molecular-weights of 100,000 and 5,000 g/mol, respectively, were synthesized by ring-opening polymerization in bulk of LLA and DLA monomers, respectively, at 165 °C for 2.5 h under a nitrogen atmosphere using stannous octoate (0.01 mol%) and 1-dodecanol as the initiating system. 1-Dodecanol contents of 0.14 and 2.8 mol% were chosen to synthesize high M.W. PLLA and low M.W. PDLA, respectively. The obtained polylactides were granulated before drying in a vacuum oven at 110 °C for 3 h.

The P(CL-co-LLA) copolyester with feed CL/LLA ratio of 60/40 mol% was synthesized by ring-opening polymerization in bulk of CL and LLA monomers 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. The yields of PLLA, PDLA and copolyester (98%, 96% and 97%, respectively) were determined
by dissolving in chloroform before precipitation with cool n-hexane followed by drying in a vacuum oven at room temperature for 24 h.

2.3. Characterization of PLLA, PDLA and copolyester

The L-enantiomer contents of PLLA and PDLA were determined at 25 °C in chloroform (1.0 g/dL) with a wavelength of 589 nm using a Bellingham and Stanley Polarimeter ADP220.

The number-averaged molecular weight (Mn) and dispersity index (DI) were measured by gel permeation chromatography (GPC) using a Waters e2695 separations module equipped with PLgel 10 µm mixed B 2 columns operating at 40 °C and employing a refractive index (RI) detector. Tetrahydrofuran was used as the solvent at a flow rate of 1.0 mL/min. Polystyrene standards were used for calibration.

Thermal transitions were determined with a Perkin-Elmer Pyris Diamond differential scanning calorimeter (DSC) under a nitrogen flow. For DSC, samples were melted at 200 °C for 3 min to remove their thermal history, and then quenched to -40 °C according to the DSC instrument’s own default cooling mode before heating from -40 to 200 °C at a rate of 10 °C/min.

The copolymer composition of copolyester was determined by 1H-NMR spectroscopy (Bruker 400 NMR spectrometer) at room temperature with tetramethylsilane as an internal standard. Deuterated chloroform (CDCl3) was used as a solvent.

2.4. Preparation of scPLA/copolyester blends

The PLLA, PDLA and copolyester were dried in a vacuum oven at 50 °C overnight to remove moisture that might influence the thermal degradation of PLLA, PDLA and copolyester [19] before melt blending using a HAAKE Polylab OS Rheomix batch mixer system at 200 °C for 4 min with a 100 rpm rotor speed. The resulting blends were granulated followed with drying in a vacuum oven at 50 °C overnight before characterization and compression molding. Influences of PLLA/PDLA ratios [100/0, 90/10, 80/20 and 70/30 (w/w)] and copolyester contents [10 and 20 wt%] were investigated. Pure PLLA without copolyester blending was also prepared by the same method for comparison.

The blend films were prepared by an Auto CH CARVER® compression molding machine at 240 °C without compression force for 1.0 min and with a compression force of 5 tons for 1.0 min. The obtained films were cooled for 1.0 min with cooling plates. The film thicknesses were approximately 0.2–0.3 mm. The resulting films were kept at room temperature for 24 h before characterization.
2.5. Characterization of scPLA/copolyester blends

The thermal transition properties of the blends were studied with a DSC. The thermal history of the samples was removed by melting at 250 °C for 3 min. Then, the sample was quenched to 0 °C before heating from 0 to 250 °C at a rate of 10 °C/min.

The phase morphology of the blend films was determined using a JEOL JSM-6460LV scanning electron microscope (SEM). The film samples were immersed in liquid nitrogen for 30 min before film fracture. The film fractures were coated with gold to enhance conductivity before scanning.

The crystalline structures of the blend films were determined with a Bruker D8 Advance wide-angle X-ray diffractometer (XRD) at room temperature using CuKα radiation at 40 kV and 40 mA. For XRD, the scanning angle range of 2θ = 5°–30° at a scan speed of 3°/min was used. The degrees of crystallinity (Xc) of the blend films for homo-crystallites (Xc,hc) and stereocomplex crystallites (Xc,sc) were estimated from XRD patterns and weight fraction of scPLA in the blends (WscPLA) as Eqs. (1) and (2), respectively.

\[
X_{c,\text{hc}} (%) = \left[ \frac{A_{\text{hc}}}{A_{\text{hc}} + A_{\text{sc}} + A_{\text{amorphous}}} \right] \times \left[ \frac{1}{W_{\text{scPLA}}} \right] \times 100 \quad (1)
\]

\[
X_{c,\text{sc}} (%) = \left[ \frac{A_{\text{sc}}}{A_{\text{hc}} + A_{\text{sc}} + A_{\text{amorphous}}} \right] \times \left[ \frac{1}{W_{\text{scPLA}}} \right] \times 100 \quad (2)
\]

where \(A_{\text{hc}}, A_{\text{sc}}\) and \(A_{\text{amorphous}}\) were peak areas of homo- and stereocomplex crystallites as well as area of underlying hump, respectively. The \(W_{\text{scPLA}}\) of 10% and 20% copolyester blend films were 0.9 and 0.8, respectively.

The tensile properties of the blend films, including stress at break, elongation at break and Young’s modulus, were determined at 25 °C with a Lloyds LRX + Universal Mechanical Testing Machine. The films with 100 × 10 mm in size were tested with a gauge length of 50 mm and a crosshead speed of 50 mm/min. The tensile properties were averaged from at least five determinations for each sample.

The thermo-mechanical properties of the blend films with \(5 \times 20 \times 0.2\) mm in size were determined with a TA Instrument Q800 dynamic mechanical analyzer (DMA) in a multi-frequency strain mode. For DMA analysis, the film samples were heated from 30 to 150 °C at the rate of 2 °C/min. The scan amplitude was set to be 10 μm and the scanning frequency was 1 Hz.

The dimensional stability to heat of the blend films was tested at 80 °C for 30 sec with a 200 g load. Initial length of film samples was kept constant at 20 mm. The dimensional stability to heat was calculated by Eq. (3).

Dimensional stability to heat (%) = \(\frac{\text{initial length (mm)}/\text{final length (mm)}}{100}\) (3)
3. Results and discussion

3.1. Characterization of PLLA, PDLA and copolyester

The characteristics of PLLA, PDLA and copolyester are summarized in Table 1. The L-enantiomer contents indicate that the obtained PLLA and PDLA had high L- and D-enantiomer contents, respectively. They had high optical purity (>95%). Therefore high M.W. PLLA and low M.W. PDLA were successfully synthesized by adjusting the 1-docanol concentration. The $M_n$ values of PLLA and PDLA from GPC were 90,000 and 5,700 g/mol, respectively. Both PLLA and PDLA were semi-crystalline. Glass transition temperature ($T_g$) and melting temperature ($T_m$) of PDLA were lower than those of PLLA because the PDLA chains were shorter than the PLLA chains. The high M.W. copolyester ($M_n$ from GPC = 85,000 g/mol) was also synthesized and was completely amorphous with a $T_g$ from DSC of −25 °C. All of the GPC curves exhibited similar unimodal dispersity of molecular weight as shown in Fig. 1.

The final CL/LLA ratio of the copolyester was determined from its $^1$H-NMR spectrum by ratioing the peak areas corresponding to the ε-methylene protons (−CH$_2$) of CL units at δ = 3.9−4.2 ppm (peak a) and the methine protons (−CH) of LLA units at δ = 5.0−5.3 ppm (peak g) as shown in Fig. 2. The final CL/LLA ratio of the copolyester from $^1$H-NMR (62/38 mol%) was nearly that of the feed CL/LLA ratio (60/40 mol%) suggesting that the copolymerization reaction had achieved near-quantitative conversion.

3.2. Characterization of scPLA/copolyester blends

In our preliminary study, copolyester-free scPLA films with PLLA/PDLA ratios of 100/0, 90/10, 80/20 and 70/30 can be prepared as continuous films by compression molding at 240 °C. However, the copolyester-free scPLA films with PLLA/PDLA ratios of 80/20 and 70/30 exhibited high brittleness. These latter films could not be cut to appropriate size for tensile and thermo-mechanical tests and had no practical use. However, the less brittle scPLA films contained 10 and 20 wt% copolyester coded as 10% and 20%copolyester blend films, respectively, reported here were

| Polymer  | L-content (%)$^a$ | $M_n$ (g/mol)$^b$ | DI$^b$ | $T_g$ (°C)$^c$ | $T_m$ (°C)$^c$ | Final CL/LLA ratio (mol%)$^d$ |
|----------|------------------|------------------|--------|---------------|---------------|-----------------------------|
| PLLA     | 96.5             | 90,000           | 2.8    | 54            | 173           | –                           |
| PDLA     | 2.9              | 5,700            | 1.9    | 47            | 160           | –                           |
| Copolyester | –               | 85,000           | 2.1    | −25           | –             | 62/38                       |

$^a$ obtained from polarimetry.

$^b$ determined from GPC curves.

$^c$ obtained from DSC curves.

$^d$ determined from $^1$H-NMR spectrum.
Fig. 1. GPC curves of (a) PLLA, (b) PDLA and (c) copolyester.
successfully prepared by the same method and could be cut to appropriate size for
tensile and thermo-mechanical tests.

3.2.1. Thermal transitions

The thermal transition properties of blends were determined from DSC thermograms
as shown in Fig. 3. The DSC results are summarized in Table 2. The $T_g$ of scPLA
matrices did not significantly change with the PLLA/PDLA ratios and copolyester
contents. It should be noted that the $T_{cc}$ peak of 10% copolyester blend with 90/10
PLLA/PDLA in Fig. 3(b) showed as a broad peak. This may be due to stereocomplex
crystallites having restricted chain mobility in both PLLA and PDLA for their homo-
crystallization. The stereocomplex crystallites were formed before homo-crystallites
during DSC heating [20]. Both the 10% and 20% copolyester blends with 70/30
PLLA/PDLA have no $T_{cc}$ peaks that could be attributed to complete crystallization
during the quenching step. This suggests that 30 wt% PDLA can induce complete
crystallization of the PLA matrix.

Fig. 2. $^1$H-NMR spectrum of copolyester (Peak-proton assignments as shown).

Fig. 3. DSC thermograms of 10% copolyester blend films with (a) 100/0, (b) 90/10, (c) 80/20, (d) 70/30
PLLA/PDLA and (e) 20% copolyester blend film with 70/30 PLLA/PDLA.
For the 10% copolyester blends, enthalpies of cold crystallization ($\Delta H_{cc}$) drastically decreased as the PDLA contents increased from 20% to 30%. This is due to stereocomplexation of PLLA/PDLA blends accelerated crystallization of PLA matrix. Also enthalpies of melting of homo-crystallites ($\Delta H_{m,hc}$) steadily decreased whereas they increased significantly in stereocomplex crystallites ($\Delta H_{m,sc}$) as the PDLA contents increased. This demonstrates the stereocomplexation of blends increased with the PDLA ratio. However, the values of $X_c$ from DSC of both the homo- and stereocomplex crystallites could not be calculated because of the $T_{cc}$ peaks of homo- and stereocomplex crystallizations overlapped each other [21].

### 3.2.2. Phase morphology

Phase separation between continuous scPLA matrix and dispersed copolyester particles of the blend films was determined from cryo-fractured surfaces as illustrated in Fig. 4. It is clearly seen that the copolyester phases were nearly spherical in shape with good distribution. The diameters of copolyester particles were less than 3.0 $\mu$m. However, the particle sizes of 20% copolyester blend film seem to be slightly larger than those of the 10% copolyester blend films. The higher copolyester content induced larger agglomerate of copolyester phases.

Good phase-adhesion between the scPLA matrix and copolyester particles in the blend films was observed. This could be explained by the L-lactide segments of copolyester chains having enhanced phase compatibility between PLA matrix and copolyester particles [22]. Therefore the stereocomplexation of PLA matrix and copolyester contents did not significantly affect phase adhesion of the blend films.

### 3.2.3. Crystalline structures

The crystalline structures of the blend films were determined from XRD patterns as shown in Fig. 5. The broad hump and peaks of XRD patterns is attributed to the diffraction profiles for amorphous and crystalline fractions, respectively. The XRD peaks of the homo-crystallites (hc) and stereocomplex crystallites (sc) were also assigned in Fig. 5 [23, 24, 25]. It can be seen that the peak intensities of sc at

| PLLA/PDLA (w/w) | scPLA/copolyester (w/w) | $T_g$ (°C) | $T_{cc}$ (°C) | $\Delta H_{cc}$ (J/g) | $T_{m,hc}$ (°C) | $\Delta H_{m,hc}$ (J/g) | $T_{m,sc}$ (°C) | $\Delta H_{m,sc}$ (J/g) |
|-----------------|------------------------|------------|--------------|-----------------------|----------------|-----------------------|----------------|-----------------------|
| 100/0           | 90/10                  | 48         | 82           | 24.2                  | 170            | 45.2                  | -              | -                     |
| 90/10           | 90/10                  | 51         | 92           | 28.1                  | 170            | 31.0                  | 216            | 14.4                  |
| 80/20           | 90/10                  | 50         | 78           | 4.5                   | 167            | 7.3                   | 220            | 27.7                  |
| 70/30           | 90/10                  | 50         | -            | -                     | -              | 218                   | 47.4           |                       |
| 70/30           | 80/20                  | 50         | -            | -                     | 165            | 3.5                   | 218            | 45.4                  |
12°, 21° and 24° increased with the PDLA contents for the 10% copolyester blend films [see Fig. 5(a)–(d)]. There are no hc peaks.

The XRD results differed from the previous DSC results. From DSC thermograms, the T_m peaks of both the hc and sc were detected for the 10% copolyester blends with 100/0, 90/10 and 80/20 PLLA/PDLA [see Fig. 3(a)–(c)]. This could be explained by

**Fig. 4.** SEM images of cross-sections of 10% copolyester blend films with (a) 100/0, (b) 90/10, (c) 80/20, (d) 70/30 PLLA/PDLA and (e) 20% copolyester blend film with 70/30 PLLA/PDLA. (All scale bars = 5.0 μm).

**Fig. 5.** XRD patterns of 10% copolyester blend films with (a) 100/0, (b) 90/10, (c) 80/20, (d) 70/30 PLLA/PDLA and (e) 20% copolyester blend film with 70/30 PLLA/PDLA.
chain mobility of PLLA and PDLA without compression force during DSC heating induced PLA homo-crystallization. In addition, stereocomplexation of the PLA matrix was enhanced by external force [14, 26]. However, the 20% copolyester blend film in Fig. 5(e) had XRD peaks of both hc (at 17°) and sc (at 12°, 21° and 24°).

The \( X_{c,\text{hc}} \) and \( X_{c,\text{sc}} \) of the blend films were determined from Eqs. (1) and (2), respectively. The pure PLLA film in Fig. 5(a) was completely amorphous. The 10% copolyester blend films with 90/10, 80/20 and 70/30 PLLA/PDLA in Fig. 5(b)–(d), respectively, had only the stereocomplex crystallites that had \( X_{c,\text{sc}} \) values of 0.96%, 6.2% and 17.1%, respectively. The \( X_{c,\text{sc}} \) values significantly increased with the PDLA contents. The \( X_{c,\text{hc}} \) and \( X_{c,\text{sc}} \) of the 20% copolyester blend film in Fig. 5(e) were 1.4% and 6.5%, respectively. This indicates the 20 wt% copolyester suppressed stereocomplexation of PLA film matrix and induced homo-crystallization.

### 3.2.4. Mechanical properties

Fig. 6 illustrates tensile properties of the blend films compared with polypropylene film. The stresses and strains at break of the 10% copolyester blend films were 18.4–24.5 MPa and 4.0–4.6%, respectively [Fig. 6(a)–(c)], except for the 10% copolyester blend films with 70/30 PLLA/PDLA [Fig. 6(d)]. The stress and strain at break of the latter film were only 3.9 MPa and 1.7%, respectively, indicating that it is highly brittle. This is due to it containing the largest low M.W. PDLA fraction (30 %wt). It is well known that the mechanical properties of polymers strongly depend on their M.W. and we expect the higher low M.W. PDLA fraction to reduce the mechanical properties of the scPLA. It has been reported that the longer chains of high M.W. PLLA and PDLA in the amorphous region form links between stereocomplex crystallites leading to improved tensile properties of scPLA [18].

However, the stress and strain at break of the 10% copolyester blend film with 70/30 PLLA/PDLA in Fig. 6(d) were improved when the copolyester was increased from 10% to 20% as shown in Fig. 6(e). This can be explained by the 20% copolyester having improved film flexibility due to its elastomer characteristic. The polypropylene film in Fig. 6(f) exhibited similar stress at break but higher strain at break with the 20% copolyester blend film in Fig. 6(e). This is due to the lower \( T_g \) of polypropylene. The Young’s moduli of all the blend films were similar in the range 784–899 MPa.

### 3.2.5. Thermo-mechanical properties

The heat resistance of the PLLA and scPLA has been widely investigated from storage modulus and tan \( \delta \) as a function of temperature by DMA analysis [27, 28, 29, 30]. The PLLA with low \( X_c \) exhibited a sharp fall of storage modulus as the temperature passed the \( T_g \) due to glassy-to-rubbery transition. The storage modulus rises again upon DMA heating due to cold crystallization of PLLA [27]. This phenomena
indicated that the PLLA with low $X_c$ had poor heat-resistance while high heat-resistance was obtained when the PLLA had a higher $X_c$. The crystalline regions of PLLA maintain stiffness of PLLA as the temperature passes the $T_g$ [30].

Fig. 7 shows storage modulus as a function of temperature for the blend films compared with the polypropylene film. The storage moduli of the 10% copolyester blend films with 100/0, 90/10 and 80/20 PLLA/PDLA in Fig. 7(a)–(c), respectively, decreased to near zero as a temperature of about 50 °C before raising up at around 70 °C during DMA heating. The storage modulus of pure PLLA film was similar the 10% copolyester blend film with 100/0 PLLA/PDLA (data not show). This suggests that they had poor heat-resistance. While the 10% and 20% copolyester blend films with 70/30 PLLA/PDLA in Fig. 7(d) and (e), respectively, had no cold-crystallization behavior after the dramatic drop of storage moduli in glassy-to-rubbery transition corresponding to the DSC results in which they lacked $T_{cc}$ peaks. The XRD and DMA results suggested that the higher $X_c$ values enhanced better heat-resistance of the blend films as has been reported in the literature [30]. Although stereocomplexation
enhanced crystallization of PLLA/PDLA blends, the minimum $X_c$ value of scPLA after molding is an important factor for improving its heat resistance in practical use. For high heat-resistant polypropylene film in Fig. 7(f), the storage modulus slowly dropped with the temperature because of its high $X_c$ value.

The $T_g$ of all the blend films from the tan δ peaks were around 55 °C as shown in Fig. 8. These were higher than the $T_g$ determined by the DSC (10 °C/min) due to a slower heating rate of DMA (2 °C/min). The area underneath the tan δ peak represents the ability of blend films to absorb and dissipate energy. This is a damping ability [29, 30]. The areas underneath the tan δ peak of the 10%copolyester blend films with 100/0, 90/10 and 80/20 PLLA/PDLA in Fig. 8(a)–(c), respectively, were greater than both the 10% and 20%copolyester blend films with 70/30 PLLA/PDLA in Fig. 8(d) and (e), respectively. This can be explained by the chain mobility of blend films with higher $X_c$ value being restricted in the glassy-to-rubbery transition.

Fig. 7. Storage modulus from DMA of 10%copolyester blend films with (a) 100/0, (b) 90/10, (c) 80/20, (d) 70/30 PLLA/PDLA, (e) 20%copolyester blend film with 70/30 PLLA/PDLA and (f) polypropylene film.

Fig. 8. Tan δ from DMA of 10%copolyester blend films with (a) 100/0, (b) 90/10, (c) 80/20, (d) 70/30 PLLA/PDLA and (e) 20%copolyester blend film with 70/30 PLLA/PDLA.
3.2.6. Dimensional stability

Determination of the dimensional stability to heat of film samples was performed at 80 °C under 200 g load for 30 sec. Fig. 9 shows film samples before and after testing. The final length of the PLLA without copolyester blending was 108.5 mm (not shown in Fig. 9). This is a little lower than the blend film in Fig. 9(a). This is due to the flexibility of rubber-like copolyester component. The dimensions of polypropylene film did not change after testing and it is well known that polypropylene film has high heat-resistance. The 10% copolyester blend film with 100/0 PLLA/PDLA in Fig. 9(a) exhibits the largest film extension due to this film being completely amorphous. The film extension slightly decreased when the PDLA contents were 10 and 20 wt% for the 10% copolyester blend films as shown in Fig. 9(b) and (c), respectively. This is due to increased values of $X_c$ as revealed from XRD results. It is interestingly that the 10% copolyester blend film with 70/30 PLLA/PDLA in Fig. 9(d) exhibited film extension similar to the polypropylene film because it had a high $X_c$. However, this film was brittle as shown by tensile test in a previous study [see Fig. 6(d)]. This brittle scPLA film is then difficult to use in practical applications. However, the more flexible 20% copolyester blend film with 70/30 PLLA/PDLA in Fig. 9(e) showed a little longer film extension because of its larger copolyester content.

Fig. 10 shows the dimensional stability to heat of the film samples as calculated from Eq. (3). The dimensional stability to heat of PLLA film was 19.9%. The 10% copolyester blend films with 100/0, 90/10, and 80/20 PLLA/PDLA in Fig. 10(a)–(c) were similar in the range 16.3–24.8%. There were low dimensional-stabilities to heat because of their low $X_c$. It is clearly seen that both the 10% and 20% copolyester

![Fig. 9. Photographs after testing of dimensional stability to heat of 10% copolyester blend films with (a) 100/0, (b) 90/10, (c) 80/20, (d) 70/30 PLLA/PDLA, (e) 20% copolyester blend film with 70/30 PLLA/PDLA and (f) polypropylene film. Average final lengths of (a), (b), (c), (d), (e) and (f) were 122.5, 102.2, 82.8, 20.5, 25.8, 20.0 mm, respectively.](image-url)
blend films with 70/30 PLLA/PDLA in Fig. 10(d) and (e), respectively, exhibited high dimensional-stability to heat similar to that of the polypropylene film in Fig. 10(f). The results suggested that the heat resistance of blend films could be significantly improved with 30 wt% PDLA.

4. Conclusions

From this research it can be concluded that the 30 wt% low M.W. PDLA induced complete stereocomplexation of the 10% copolyester blends as revealed by DSC. However the 10% copolyester blend film with 70/30 PLLA/PDLA was brittle. Increasing copolyester contents from 10 to 20 %wt can improve film flexibility. The copolyester showed good phase adhesion with the film matrix. From XRD, the 10% copolyester blend films exhibited only stereocomplex crystallites. The homo-crystallites were also formed when the copolyester content was 20 wt%. The 10% and 20% copolyester blend films with 70/30 PLLA/PDLA showed relatively high thermo-mechanical properties. The latter films exhibited high dimensional-stability to heat similar to that of polypropylene film. This research could provide guidance toward preparation of high heat-resistant scPLA products using melt blending before compression molding.

Declarations

Author contribution statement

Yaowalak Srisuwan: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data.

Yodthong Baimark: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Wrote the paper.
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Competing interest statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

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