Thermal analysis on phase behavior of poly(L-lactic acid) interacting with aliphatic polyesters

Ya-Ting Hsieh · Nai-Tzu Kuo · Eamor M. Woo

Abstract Thermal behavior, miscibility, and crystalline morphology in blends of low-molecular-weight poly (L-lactic acid) (LM$_w$-PLLA) or high-molecular-weight PLLA (HM$_w$-PLLA) with various polyesters such as poly(butylene adipate) (PBA), poly(ethylene adipate) (PEA), poly(trimethylene adipate) (PTA), or poly(ethylene succinate) (PESu), respectively, were explored using differential scanning calorimeter (DSC), and polarized-light optical microscopy (POM). Phase behavior in blends of PLLA with other polyesters has been intriguing and not straight forward. Using a low- and high molecular weight PLLA, this study aimed at mainly using thermal analyses for probing the phase behavior, phase diagrams, and temperature dependence of blends systems composed of PLLA of two different molecular weights (low and high) with a series of aliphatic polyesters of different structures varying in the (CH$_2$/CO) ratio in main chains. The blends of LM$_w$-PLLA/PEA and LM$_w$-PLLA/PTA show miscibility in melt and amorphous glassy states. Meanwhile, the LM$_w$-PLLA/PESu blend is immiscible with an asymmetry-shaped upper critical solution temperature (UCST) at 220–240 °C depending on the blend composition. In contrast to miscibility in LM$_w$-PLLA/PTA and LM$_w$-PLLA/PEA blends, HM$_w$-PLLA with polyesters are mostly immiscible; and HM$_w$-PLLA/PTA blend is the only one showing an asymmetry-shaped UCST phase diagram with clarity points at 195–235 °C (depending on composition). Reversibility of UCST behavior, with no chemical transreactions, in these blends was proven by solvent recasting, gel permeation chromatography, and Fourier transform infrared spectroscopy (FT-IR). Crystalline morphology behavior of the LM$_w$-PLLA/PEA and LM$_w$-PLLA/PTA blends furnishes addition evidence for miscibility in the amorphous phase between LM$_w$-PLLA and PTA or PEA.

Keywords Miscibility polyesters · Crystalline morphology · PLLA · UCST

Introduction

Thermal transitions and phase behavior in polymer blends can be temperature dependent, as revealed in common upper critical solution temperature (UCST) or lower critical solution temperature (LCST) phenomena. UCST behavior is normally seen in blends of polymers possessing similar chemical structures or functional groups. Polymer blends that are thermodynamically immiscible at lower temperatures but turn miscible at elevated temperatures (UCST) have been known in some well-studied classical blends of two alike polymers, such as blends of polystyrene (PS) with poly(α-methyl styrene) (PαMS) [1–7]. Recently, biodegradable polyesters are finding increasingly more applications for environmental concerns. Their blends with other polymers have been attempted for variety of different applications. Blend of poly(methyl methacrylate) (PMMA) with poly(L-lactic acid) (PLLA) has been commercially developed. Although the PMMA/PLLA mixtures of all compositions can be processed in melt followed with quenching to ambient to preserve the PMMA/PLLA blend into a quasi-miscible state, it has been proven that the PMMA/PLLA blend actually exhibits UCST behavior [8], which means that it is not thermodynamically miscible at low temperatures (including ambient) but it turns into a miscible mixture upon heating to a certain high temperature

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governed by thermodynamic driving force known as Gibb's free energy of mixing (ΔG_{mix}). The "quasi-miscible" blends of PMMA/PLLA can be thermodynamically reverted back to immiscibility by dissolving the blend into solvent and re-casting, which has been experimentally proven [8]. Other miscible or partially miscible blends comprising PLLA have been developed, such as PDLLA/PLLA, PDLA/PLLA [9–11], poly(3-hydroxybutyric acid) (PHB)/PLLA [12–14], PMMA/PLLA [15], poly(p-vinyl phenol) (PVPh)/PLLA [16], poly(vinyl acetate) (PVAc)/PLLA [17], poly(ethylene oxide) (PEO)/PLLA [18], etc.

Blending of PLLA with other polyesters is one of approaches to modify the properties of PLLA. However, such modification by blending with other polyesters mostly leads to immiscible mixtures, owing to the fact that the interaction between PLLA and other polyesters is generally weak or insufficient for leading to a homogeneous mixture. For example, the blend of poly(ethylene succinate) (PESu) with PLLA was claimed to be immiscible [19]. However, in a later study, it was found that the blend of PESu with PLLA ($M_w = 150000$ g mol^{-1}) actually exhibited a UCST phase boundary at a quite high temperature of ~ 260 °C [20], which means that the blend PESu with PLLA is immiscible at low temperatures but its phase can transform into miscible homogeneity upon heating to certain high temperatures known as UCST. In addition, Doi et al. [21] reported that PHB was immiscible with poly(ethylene adipate) (PEA), and phase domains in the PHB/PEA blends were seen up to 200 °C. The phase behavior in polyester blends may be M_w-dependent as well as temperature dependent. As M_w of PLLA is lower, blend of LM$_w$-PLLA with PESu or PEA may be different, and the blends may also undergo phase transformation with respect to temperature. Some of the PLLA or PHB blends with other polyesters might be phase-separated systems, but actually they may turn into one-phase domain when kept at above certain temperature range (UCST) or they may become miscible if the molecular weights of either or both components are lowered. This result is similarly in agreement with theoretical predictions and has been proven in many studies, or more specifically those by Domb [22] and Koyama et al. [23], who have shown that decreasing the molecular weights of polymer constituents favors blend miscibility.

In continuing and extending an earlier concurrent work on phase and thermal behavior of mixtures of PHB with series of polyesters [24], this study further probed possible differences between PLLA/polyesters and PHB/polyesters systems, i.e., effects of molecular weights and structures of either or both components in the blends. Our present study aimed at probing the phase behavior, phase diagrams, and temperature dependence of blends systems composed of PLLA of two different molecular weights (low and high) with a series of polyesters of different structures. In addition, effect of interactions between PLLA and polyesters on the morphology was analyzed.

Experimental

Materials and procedures

Poly(L-lactic acid) of a relatively low molecular weight (LM$_w$-PLLA) was purchased from Polysciences, Inc. (USA) (Catalog #18580, [L] $\sim 100\%$), with $M_w = 11000$ g mol^{-1} (GPC), $T_g = 45.3$ °C, and $T_m = 155$ °C. Another grade of PLLA with $M_w = 119400$ g mol^{-1} (HM$_w$-PLLA) was obtained from NatureWorks (6201D, [L] = 98.5%), with $T_g = 58.8$ °C, and $T_m = 165$ °C. Several polyesters of different structures were used. Poly(1,4-butylene adipate), PBA, was obtained from Aldrich, with $M_w = 12000$ g mol^{-1}, $T_g = -68$ °C, $T_m = 54$ °C, $T_d = 250$ °C. Poly (trimethylene adipate) (PTA) was obtained from Scientific Polymer Products (SP^2), Inc. (New York, USA), with $M_w = 8900$ g mol^{-1}, $T_g = -60$ °C, $T_m = 38$ °C. PEA was from Sigma-Aldrich Inc. (USA), with $M_w = 10000$ g mol^{-1}, $T_g = -50$ °C, $T_m = 45$ °C. PESu was from SP^2 (USA), with $M_w = 10000$ g mol^{-1}, $T_g = -19$ °C, $T_m = 102$ °C. The molecular weights for most polyesters in this study are high enough to be ~ 10000 g mol^{-1}. T_g's of these polyesters are between -68 and -19 °C, which are quite far enough away from that of PLLA (45–60 °C).

Scheme 1 Chemical structures of PLLA, PBA, PTA, PEA, and PESu

Blend samples of PLLA/polyester were prepared using solvent-mixing, followed with film casting. Chloroform (CHCl$_3$) was chosen as a solvent for blending. 4 wt% of two polymers (PLLA and polyester) was dissolved in the solvent and well stirred in flasks kept just below 40 °C. Solvent in polymer mixtures during film casting was first allowed to evaporate by convection under hood for 24 h.

Apparatus and procedures

Optical microscopy (OM)

Polarized-light microscope (Nikon, Optiphot-2-POL) equipped with a charge-coupled device (CCD) digital camera, was used for observing the phase structure of as-cast blends and for monitoring phase transition of blends upon heating. Blend samples were cast as thin films (solvent cast at controlled temperatures and vacuum drying) and placed on a microscope heating stage (Linkam, THMS-600 with TP-92 temperature programmer) for OM examination. Recording of UCST in blends was monitored at heating rate of 2 °C min^{-1} from ambient to phase transition. For the morphology observation, the cast-films of PLLA/polyester blends with were first melted on a hot stage at 190 °C for 2 min, and then were rapidly transported to the microscopic heating stage pre-set at desired T_c. The purpose was to quickly bring the samples to a designated isothermal temperature, with minimum temperature lag.

Differential scanning calorimetry (DSC)

Thermal transitions of blends were characterized with a differential scanning calorimeter (Perkin-Elmer, DSC-7) equipped with an intracooler for quenching. Before each T_g measurements, samples were first uniformized in DSC cells (furnace and sample holders) by heating to about 180 or ~250 °C for 1 min and quenched to sub-ambient (−50 or −60 °C) before initiating the second scans at 20 °C min^{-1}. DSC traces were recorded as the second scans. Prior to DSC runs, the temperature and heat of transition of the instrument were calibrated with indium or zinc standards. A continuous nitrogen flow in the DSC sample cell was maintained.

Fourier transform infrared spectroscopy (FT-IR)

Fourier transform infrared spectroscopy (FT-IR) (Nicolet, Magna-560) was used for discerning if there were possible molecular interactions between the constituents upon heating. Spectra were obtained at 4 cm^{-1} resolution and averages of spectra were obtained from at least 64 scans (for enhanced signals) in the standard IR wavenumber range 500–3200 cm^{-1}. Blend samples for IR measurements were cast as thin films with uniform thickness directly on KBr pellets at ambient temperature. Subsequently, IR measurements were performed on the samples cast on KBr pellets.

Gel permeation chromatography (GPC)

Gel permeation chromatography (GPC) (Waters, with RI detector) was used for discerning if there were changes in molecular weights caused by thermal degradation and/or molecular interactions between the constituents upon heating. Calibration was performed using polystyrene standards.

Results and discussion

UCST phase behavior

Blends of PLLA with polyesters were preliminarily examined for phase transition upon heating using an OM hot stage. The OM graphs for as-cast LM$_w$-PLLA/PEA and LM$_w$-PLLA/PTA = 80/20 at ambient were initially filled with crystals and small spherulites; however, upon heating the samples to T = 160 °C (above T_m of LM$_w$-PLLA), the crystals melted and the blends turned into a homogeneous phase at T = 160 °C, and they remained homogeneous upon further heating from 160 to ~250 °C. These results indicate that without the solvent induced PLLA/polyester crystals, the blends in the amorphous state were homogeneous. Proving evidence for homogeneity using the T_g criteria will be discussed in latter sections. Blend of LM$_w$-PLLA with PBA was found to be immiscible at all temperatures up to degradation near 270 °C. For the LM$_w$-PLLA/PESu blend, however, phase transition is different from the other blends.

For details on phase transitions, Fig. 1 shows illustrative OM graphs for as-cast LM$_w$-PLLA/PESu (80/20) blend upon heating from ambient to 160 °C then gradually a maximum 250 °C (at ~2 °C min^{-1}). The LM$_w$-PLLA/PESu blend at ambient were initially filled with crystals and small spherulites. Upon heating the samples to T = 160 °C (above T_m of LM$_w$-PLLA), the crystals melted, but the blend is still phase separated as evidenced by the apparent domains. However, the LM$_w$-PLLA/PESu (80/20) blend eventually achieved a homogeneous state with no visible domains upon further heating to 225 °C, and remained free of domains to ~250 °C. Further similar experiments of heating using OM hot stage yielded that the transition temperature varied with the blend compositions. For brevity, not all OM results for other blend compositions are shown here. In all, the LM$_w$-PLLA/PESu blend samples might go through a thermodynamic phase transition from separation to homogeneous phase upon heating, which is known as UCST behavior.

Figure 2 summarizes the result of UCST for LMw-PLLA/PESu of all compositions. The "clarity point" is defined as the temperature at which the blend samples turn from phase separation (cloudy) into homogeneity with no domains (clear), which apparently depends on the blend compositions. The maximum point is known as the UCST = 240 °C, whose physical meaning is that the

Fig. 1 OM graphs for as-cast LM$_w$-PLLA/PESu = 80/20 blend upon heating
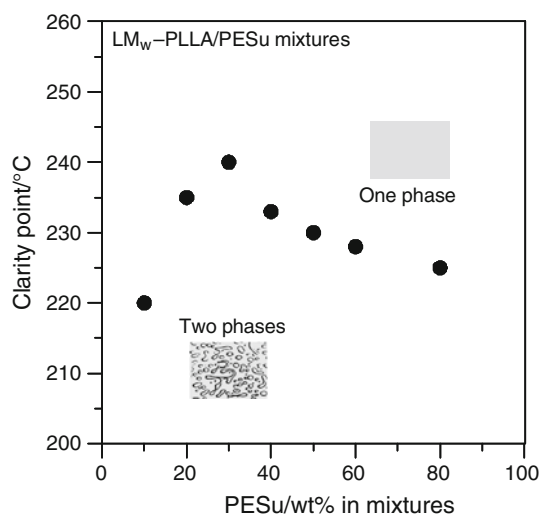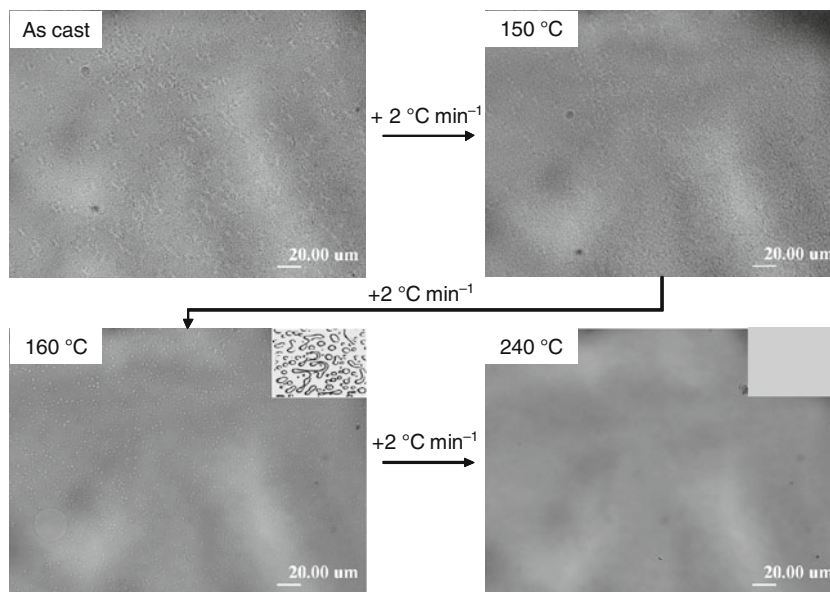

Fig. 2 Phase diagram showing UCST for LM$_w$-PLLA/PESu mixtures as a function of composition

blends of all compositions will be one phase at or above this temperature. The asymmetry in the UCST phase curve is expected due to the difference in molecular weight distributions in these two constituents.

UCST phase behavior with reversibility

As discussed, the LM$_w$-PLLA/PESu blend is a UCST system; thus, rapid quenching of the blend from above USCT was expected to freeze the blends state into a quasi-miscible state. Subsequent DSC scanning on the quenched blend samples was performed to reveal T_g behavior. As a demonstration, proof of UCST behavior and reversibility for the LM$_w$-PLLA/PESu blend was elaborated. Figure 3
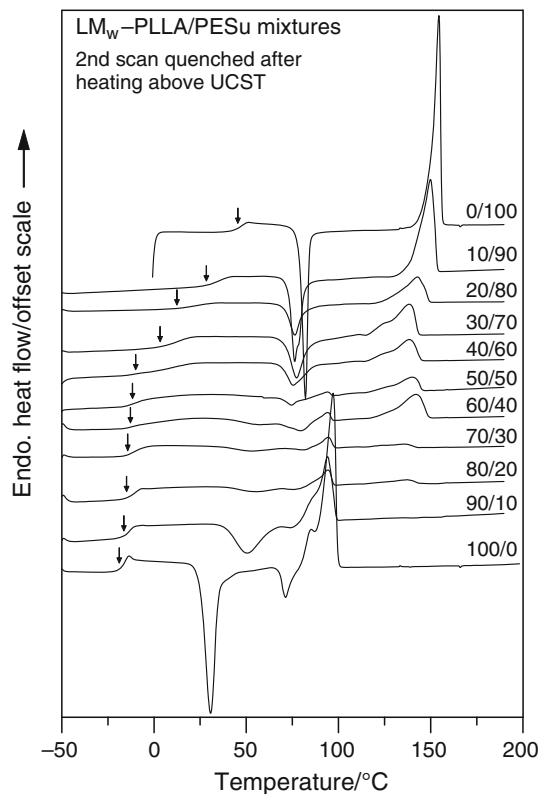
Fig. 3 DSC curves for LM$_w$-PLLA/PESu blend of different compositions: 2nd scan after quenching from UCST

shows DSC curves for LM$_w$-PLLA/PESu blend of different compositions. The DSC traces were all 2nd scans on the samples after they were heated to ~250 °C (UCST = 240 °C) briefly, then rapid quenched to sub-ambient to freeze the homogeneous state. All DSC traces show a single composition-dependent T_g for all compositions.
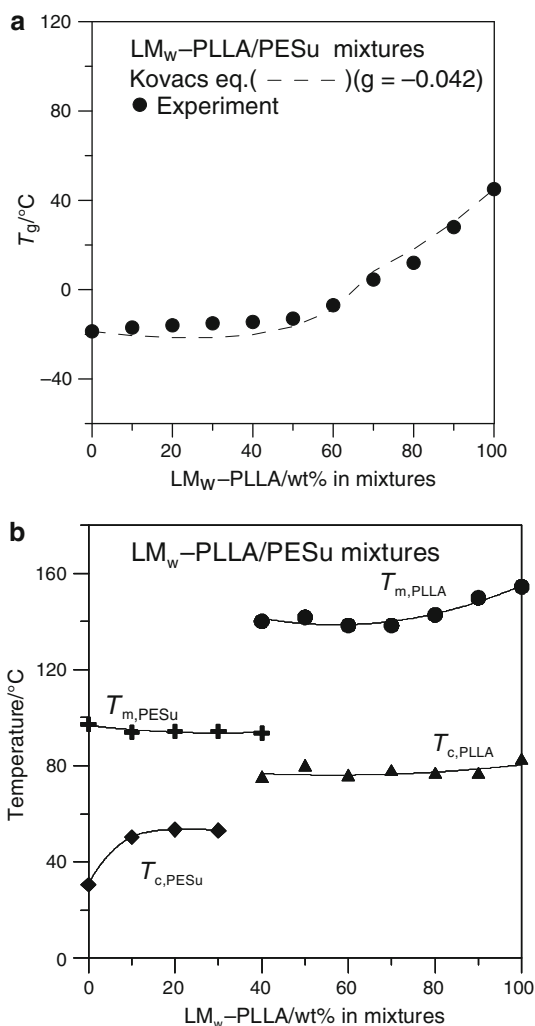
Fig. 4 a T_g versus composition for LM$_w$-PLLA/PESu mixtures. **b** Apparent melting point (T_m) and cold-crystallization peak temperature (T_c) in LM$_w$-PLLA/PESu blend

Figure 4 shows T_g versus composition for LM$_w$-PLLA/PESu mixtures (Fig. 4a), and apparent melting point (T_m) and cold-crystallization peak temperature (T_c) in LM$_w$-PLLA/PESu blend (Fig. 4b). The T_g–composition relationship in Fig. 4a exhibits a cusp at an intermediate blend composition (70/30). Note that the T_g–composition relationship for the quasi-miscible LM$_w$-PLLA/PESu blend is significantly different from that for LM$_w$-PLLA/PTA or LM$_w$-PLLA/PEA blend. Classically, such cases with an abrupt cusp in T_g versus composition are best fitted by the classical Kovacs equation [25]. Miscible blend systems that exhibit a "cusp" in T_g–composition relationships are not limited to those comprising a crystalline polymer and an amorphous polymer as two constituents. It is known that miscible blends of two fully amorphous polymers are also possible to display such cusp behavior in their T_g–composition relationships. The fact suggests that the cusp/

asymmetry has no thing to do with residual crystallinity in one of the polymer components in blends. The Kovacs model [25] for blends' T_g was thus used to explain the discontinuity and apparent asymmetry in the T_g–composition relations for the quasi-miscible LMw-PLLA/PESu blends. According to the theory, if the difference of T_g between the two neat polymers ($T_{g,1}$ for PESu and $T_{g,2}$ for PLLA) is larger than 50 °C, there is a critical temperature (T_{cr}) where the contribution of free volume of the polymer with the higher T_g is zero. The corresponding critical temperature (T_{cr}) and the constituent-2 volume fraction ($\phi_{c,2}$) at which this occurs were estimated as following:

$$T_{cr} = T_{g,2} - \left(\frac{f_{g,2}}{\Delta \alpha_2}\right) \tag{1}$$

$$\phi_{c,2} = \frac{f_{g,2}}{\Delta \alpha_1 (T_{g,2} - T_{g,1}) + f_{g,2}\left(1 - \frac{\Delta \alpha_1}{\Delta \alpha_2}\right)} \tag{2}$$

where f_g is the free volume fraction at the glassy state, and $\Delta \alpha_i$ is the thermal expansion coefficient difference of the respective constituent polymer between the glassy and rubbery states. The approximately $\Delta \alpha_i$ value can be measured by $\Delta \alpha_i = 0.113/T_g$ [26, 27]. Depending on two situations, the blends' T_g is given by the following:

$$T_{g,x} = \frac{\phi_1 \Delta \alpha_1 T_{g,1} + \phi_2 \Delta \alpha_2 T_{g,2} + g\phi_1\phi_2}{\phi_1 \Delta \alpha_1 + \phi_2 \Delta \alpha_2} \quad (\text{for } T_g > T_{cr}) \tag{3}$$

$$T_{g,x} = T_{g,1} + \frac{\phi_2 T_{g,2} + g\phi_1\phi_2}{\phi_1 \Delta \alpha_1} \quad (\text{for } T_g < T_{cr}) \tag{4}$$

In this equation, g is the parameter of interactions between the components and can be related to the excess volume. The relationship is defined as:

$$g = \frac{V_e}{V\phi_1\phi_2} \tag{5}$$

where V is the molar volume of the blend, and V_e the excess molar volume. The sign of the interaction parameter g depends on that of the excess volume (V_e). A negative g value is generally taken to imply that the interactions between the dissimilar components are stronger than or at least equal to the average of those between the same molecules, and thus is favorable for miscibility.

Best fitting with the model led to $g = -0.042$ for the LMw-PLLA/PESu blend. The negative value of g indicates that interacting strengths are on average slightly greater than those between PLLA–PLLA and polyester–polyester, leading to weak but favorable interactions for a homogeneous state. In addition, Fig. 4b shows phase diagrams where the apparent melting points (T_m) and cold-crystallization peak temperatures (T_c) for two constituents (PLLA and PESu) in the quasi-miscible LM$_w$-PLLA/PESu blend

are plotted as functions of compositions. These thermal transitions, though qualitative only, yield some information about interactions between PLLA and PESu polyester.

LM$_w$-PLLA/PESu blend sample was heated to UCST, then cooled -2 °C min^{-1} from UCST = ~240 to 160 °C (above T_m of LM$_w$-PLLA but below UCST). When cooled from UCST to 160 °C, the blend did not revert immediately back to phase separation. However, this might be due to chain mobility highly retarded by viscosity. Scientific rigor may require proof that the UCST behavior is a truly physical thermodynamic process without chemical reactions, such as trans-esterification, etc., leading to the observed phase changes upon heating. Instead, the UCST-quenched homogeneous blend was dissolved in solvent, re-cast to films, which was then characterized using OM. Apparently, the UCST behavior in the blend could be made to be reversible when viscosity was reduced by solvent. Chemical reactions are not responsible for the phase homogeneity of blend upon heating. If any chemical reactions were the factors for phase transition into blend homogeneity, then the UCST-quenched blend could not have been reverted back to original phase separation by solvent re-dissolving. Figure 5 shows OM graphs for recast samples of UCST-quenched LM$_w$-PLLA/PESu = 80/20 (wt%) blend upon heating from ambient to 150 °C (below T_m of LM$_w$-PLLA crystals), 165 °C (above T_m of LMw-PLLA crystals), and finally 230 °C (above clarity point). Similar to the results shown in Fig. 2 earlier, the recast UCST-quenched LM$_w$-PLLA/PESu blend at ambient were initially filled with phase domains and tiny crystals and small spherulites. Upon heating the samples to $T = 165$ °C (above T_m of LM$_w$-PLLA), the LM$_w$-PLLA crystals completely melted, but the phase domains are apparent (shown as scheme insert for clarity). This indicates that the UCST-quenched LM$_w$-PLLA/PESu blend, quenched and locked into a homogeneous state at UCST, was reverted back to phase separation by solvent dissolution. The re-cast LM$_w$-PLLA/PESu (80/20) blend upon further heating eventually achieved a homogeneous state with no visible domains upon further heating to 230 °C, and remained free of domains. Other compositions upon heating to UCST and recasting were found to behave similarly to the 80/20 blend; for brevity, not all compositions are shown and discussed here.

Thermal characterization

Thermal analysis was performed to reveal T_g, T_c, and T_m in the PLLA/polyester blends of several compositions. Figure 6 shows DSC curves for LM$_w$-PLLA/PEA blends of different compositions (Fig. 6a), and T_g versus composition relationship for the LM$_w$-PLLA/PEA blends (Fig. 6b). Most miscible binary blends are of this type, and they usually follow a relationship as described by the classically known Fox equation [27]:

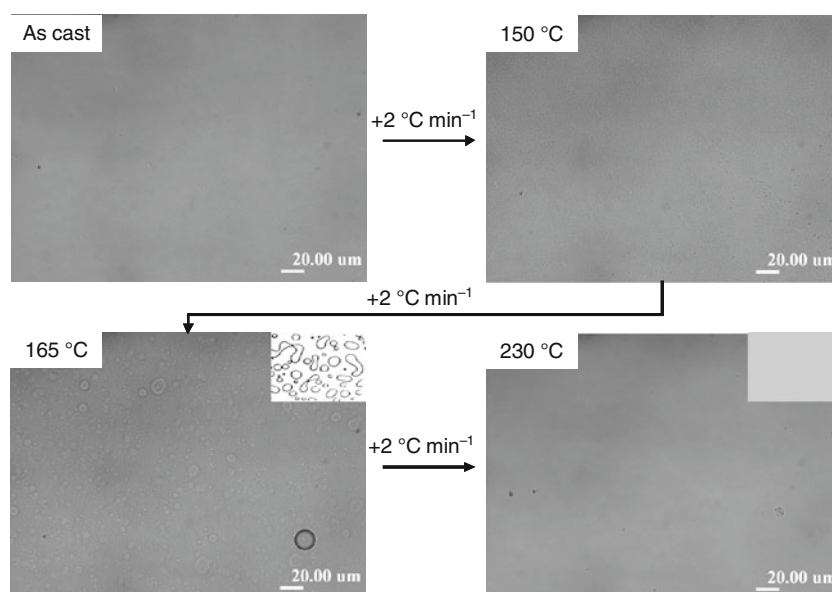$$\frac{1}{T_g} = \frac{W_1}{T_{g,1}} + \frac{W_2}{T_{g,2}} \tag{6}$$

or Gordon–Taylor equation [28]:

$$T_g = \frac{W_1 T_{g,1} + k W_2 T_{g,2}}{W_1 + k W_2}. \tag{7}$$

Fitting of the data apparently is better with the Gordon–Taylor T_g model with $k = 0.38$.

Figure 7 shows DSC curves for the LM$_w$-PLLA/PTA blend of different compositions: 2nd scan (Fig. 7a), and T_g

Fig. 5 OM graphs for recast samples of UCST-quenched LM$_w$-PLLA/PESu = 80/20 (wt%) blend upon heating
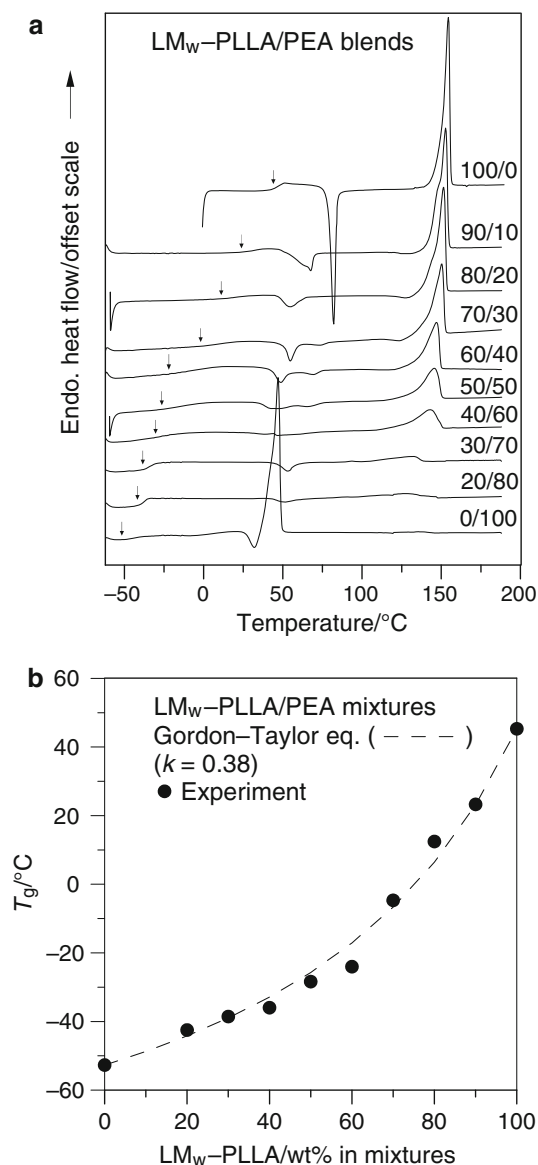
Fig. 6 a DSC curves for the LM_w-PLLA/PEA blend of different compositions: 2nd scan. **b** T_g versus composition for the LM_w-PLLA/PEA blends
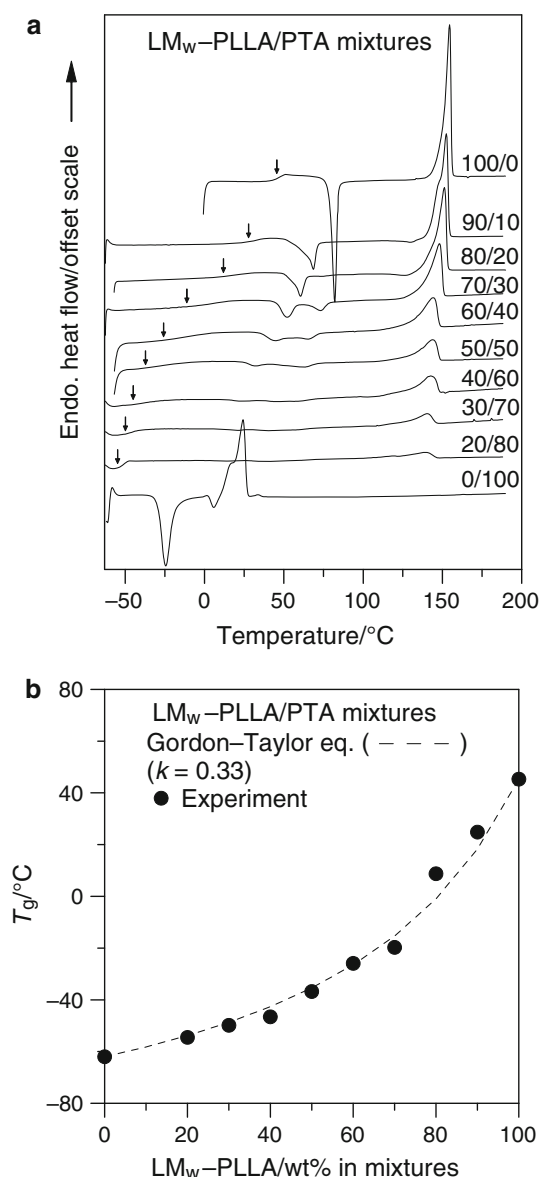

Fig. 7 a DSC curves for the LM_w-PLLA/PTA blend of different compositions: 2nd scan; **b** T_g versus composition for the LM_w-PLLA/PTA blends

versus composition relationship for the LM_w-PLLA/PTA blends (Fig. 7b). The T_g versus composition relationship shows a negative deviation from linearity for all compositions. The relationship with significant negative deviation was not described by the Fox equation. In similar approach to that in the previous figure, fitting of the T_g data with the Gordon–Taylor T_g model led to $k = 0.33$ for LM_w-PLLA/PTA blend. The fitted Gordon–Taylor equation k parameter for the LM_w-PLLA/PTA blend is close to that for LM_w-PLLA/PEA blend, indicating that the T_g behavior for these two miscible systems is comparable.

Increase in molecular weights in either PLLA or polyesters led to apparent immiscibility. HM_w-PLLA with

PESu, PEA, and PBA were found to be immiscible with phase separated domains upon heating to 220–250 °C. Figure 8 shows HM_w-PLLA/PTA blend phase behavior: Fig. 8a OM graphs showing domains at various temperatures, Fig. 8b phase boundary and UCST curves. The OM graphs in Fig. 8a show that domains in the HM_w-PLLA/PTA blend (50/50) are apparent and persist between T_m up to 180 °C; upon further heating to nearly 240 °C, the domains disappear and the blend becomes one-phase. All other blend compositions behaved similarly upon heating. Figure 8b shows UCST = 235 °C is the maximum temperature of all clarity points. The phase behavior of HM_w-PLLA/PTA blend with a UCST is significantly different

Fig. 8 HM_w-PLLA/PTA blend phase behavior: **a** OM graphs showing domains at various temperature, **b** phase boundary and UCST curves
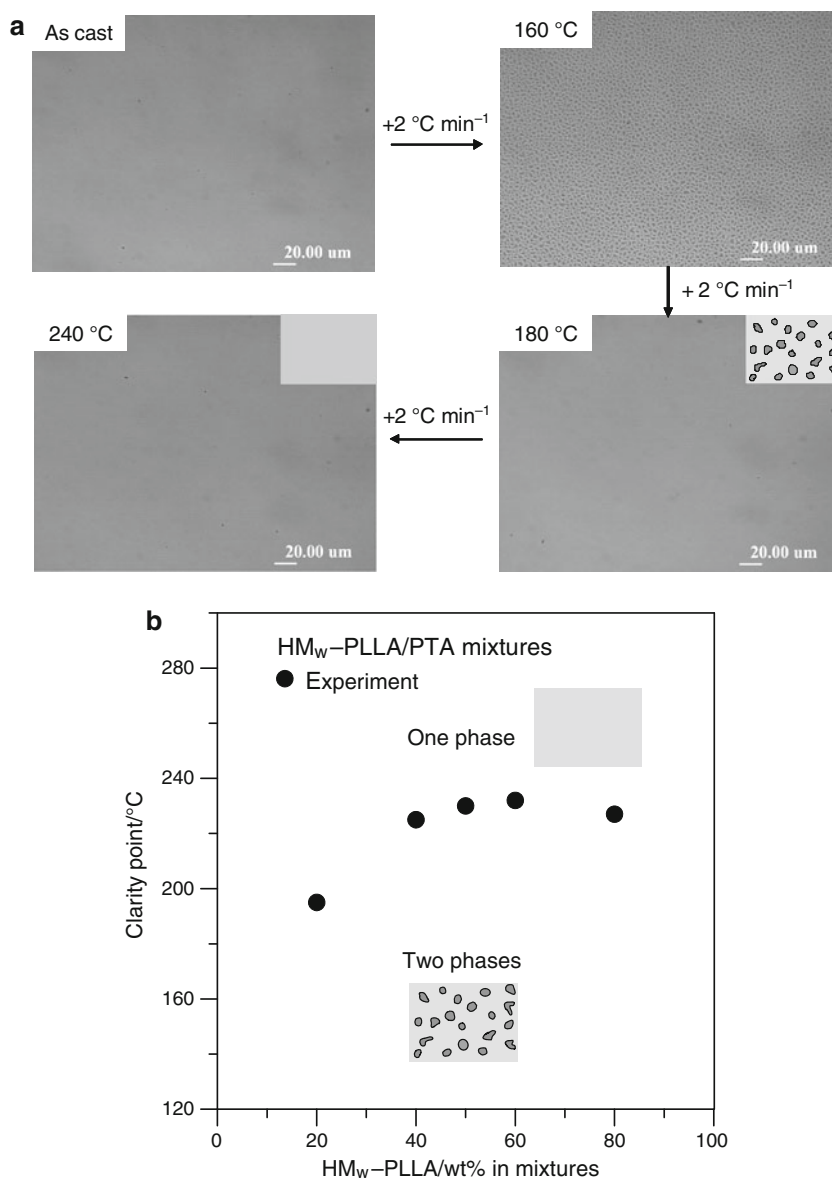
from LM_w-PLLA/PTA, even though the constituent polymers in these two blends do not change their chemical structures. This fact indicates that increase in the molecular weight of either of polymers, PLLA in this case, tends to decrease the free energy driving force for mixing.

Figure 9 shows DSC curves: 2nd scans after quenching from UCST (Fig. 9a), and T_g versus composition relationship for the HM_w-PLLA/PTA blend (Fig. 9b). The DSC traces reveal that the UCST-quenched HM_w-PLLA/PTA blend exhibits a composition-dependent single T_g for all composition range investigated, indicating that quenching from UCST did freeze the mixtures into a quasi-miscible glassy state. The T_g data were then plotted versus blend composition. Figure 9b shows that the T_g–composition relationship in for the UCST-quenched HM_w-PLLA/PTA blend exhibits a cusp at an intermediate blend

composition (60/40). Note that the T_g–composition relationship for the quasi-miscible HM_w-PLLA/PTA blend is similar to the UCST-quenched LM_w-PLLA/PESu (quasi-miscible), but is significantly different from that for the miscible LM_w-PLLA/PTA or LM_w-PLLA/PEA blend. Again, the Kovacs equation [25] was fitted, and the result led to $g = -0.032$. The negative value of g indicates that interacting strengths are on average greater than those of PLLA–PLLA and polyester–polyester.

Note that one might be concerned about thermal degradation of samples upon heating to UCST. Possibility of thermal upon heating the blend samples to elevated temperatures was doubly checked. Figures 10 and 11 show GPC and FT-IR analysis results on HM_w-PLLA/PTA (50/50) and LM_w-PLLA/PESu (50/50) blend samples, respectively, that had been similarly heated as those in DSC. The
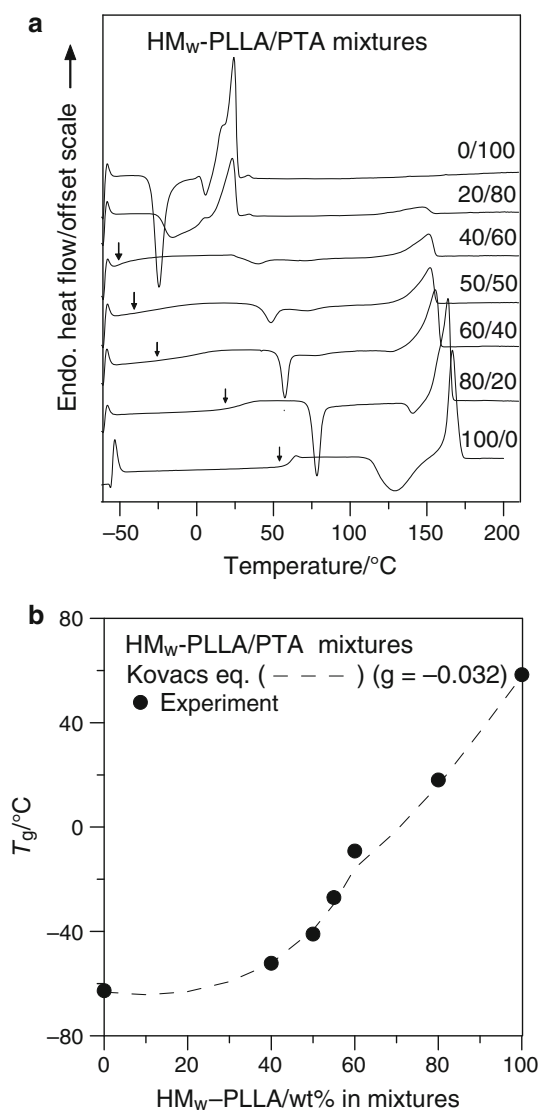
Fig. 9 **a** DSC curves: 2nd scans after quenching from UCST. **b** T_{g} versus composition relationship for HM_{w}-PLLA/PTA blends

results show no signification changes in M_{w} or chemical structures of the samples upon heating to 240 °C for around 1 min. For morphology and thermal behavior observations on the miscible blend systems with low M_{w}, T_{max} for melt treatment on samples was only at ca., 190 °C, which is much lower than TGA-determined initiation point of thermal degradation of 250 °C.

Crystalline morphology in neat LM_{w}-PLLA and blends

The interaction between two constituents of a miscible system is expected to influence the crystalline behavior. Spherulite morphology of the neat LM_{w}-PLLA was examined for future comparison with blends of LM_{w}-PLLA with other polyesters. Figure 12 shows POM morphology of neat LM_{w}-PLLA spherulites melt-crystallized
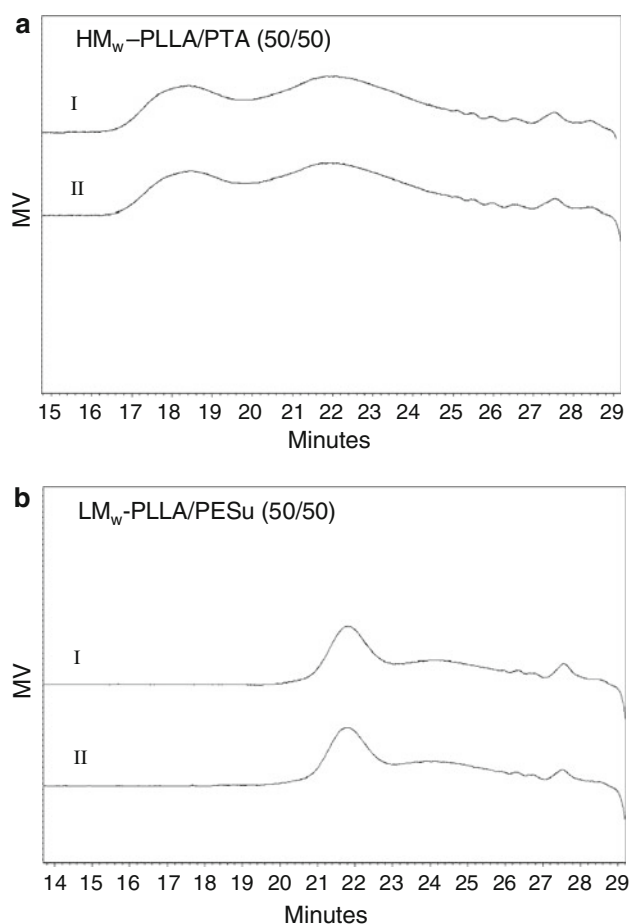
Fig. 10 GPC curves for: **a** HM_{w}-PLLA/PTA (50/50), **b** LM_{w}-PLLA/PESu (50/50) blend samples. (*I*) as-cast, (*II*) after heating to 240 °C then quenched

at various T_{c} (110–130 °C). All samples were covered with a top glass slide for film uniformity. Neat LM_{w}-PLLA, crystallized at 120 °C or lower, exhibits ringless spherulites with distinct Maltese-cross extinction. Only when crystallized at the narrow range of 122–128 °C, the spherulites in neat PLLA are characterized with concentric ring bands of varying inter-ring spacing. When crystallized at 130 °C or higher, the spherulites become ringless again.

The crystalline morphology of PLLA in two miscible blends, PLLA/PTA and PLLA/PEA, was examined. Figure 13 shows POM graphs for spherulites in LM_{w}-PLLA/PEA (80/20) blend (Fig. 13a), in comparison to LM_{w}-PLLA/PTA (80/20) blend (Fig. 13b) melt-crystallized at T_{c} as indicated (110–126 °C). As LM_{w}-PLLA and polyester are in a miscible phase, the T_{c} range within which ring bands are present in spherulites is different from that for neat LM_{w}-PLLA. The results show that when crystallized at 110–120 °C, the LM_{w}-PLLA/PEA (80/20) blend exhibits ring-banded spherulites, while for $T_{\mathrm{c}} = 126$ °C or higher, the spherulites in the blend become ringless. Similar changes are observed in the LM_{w}-PLLA/PTA (80/20)

Fig. 11 FTIR spectra for:
a HM$_w$-PLLA/PTA (50/50),
b LM$_w$-PLLA/PESu (50/50)
blend samples. (*I*) as-cast, (*II*)
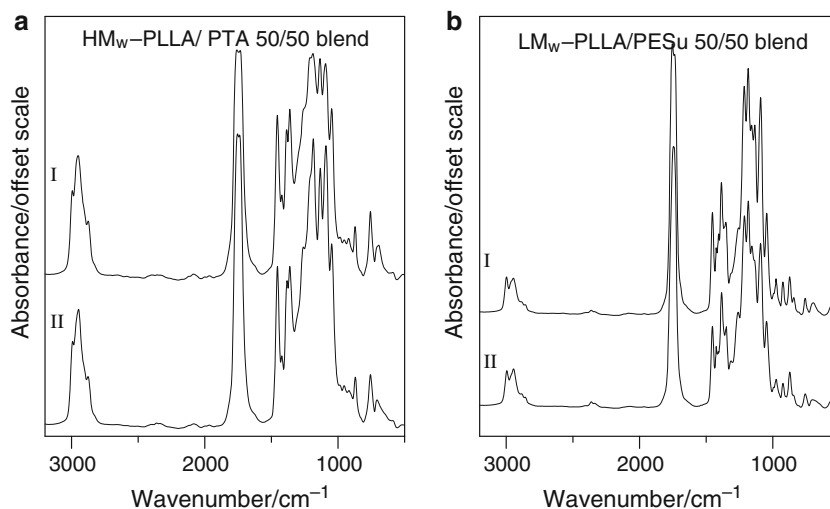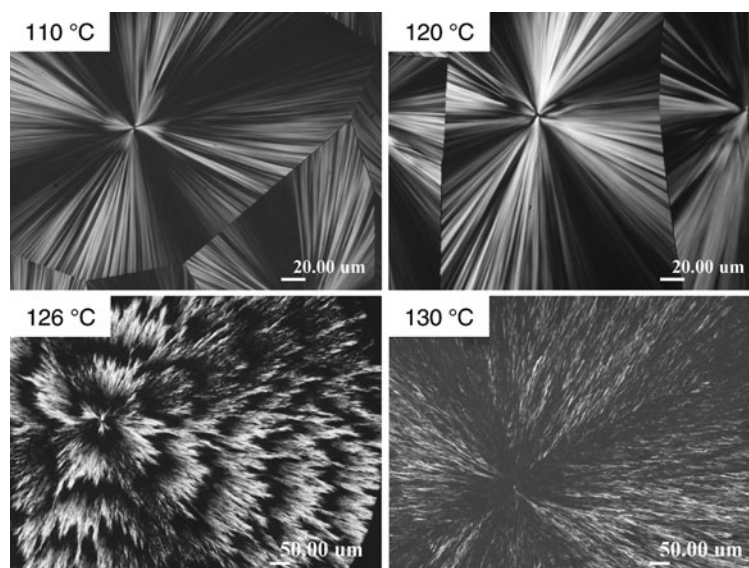after heating to 240 °C then
quenched

Fig. 12 POM graphs for
spherulite morphology of neat
LM$_w$-PLLA melt-crystallized at
T_c as indicated

blend. In general, for the LM$_w$-PLLA/PEA or LM$_w$-PLLA/PTA blends, with increasing PEA or PTA contents in blends, the lower limit for formation of ring bands is shifted to a lower temperature and the range of crystallization temperature within which ring bands in blends of any compositions appear is increasingly wider, in comparison to the temperature range of ring-banded spherulites for neat LMw-PLLA.

Miscibility in the amorphous phase of the blend can apparently influence the crystalline behavior of either or both crystalline constituent in the blend. The banding behavior of LMw-PLLA in two miscible blends, LMw-PLLA/PTA and LMw-PLLA/PEA, was examined. Figure 14 shows the temperature range for formation of ring-banded spherulites in LM$_w$-PLLA/PEA blend (Fig. 14a), in comparison with LM$_w$-PLLA/PTA blends (Fig. 14b). The upper and lower T_c bounds for formation of

ring bands in neat LM$_w$-PLLA are a narrow range of 122–128 °C. By comparison, with 20 wt% PEA in the mixture for LM$_w$-PLLA/PEA (80/20) blend composition, the T_c range for formation of ring bands widens up to 106–124 °C, with the lower limit of the T_c range shifts down to 106 °C (in comparison to 122 °C as the lower bound for neat LM$_w$-PLLA). For LM$_w$-PLLA/PEA blends of other compositions (50, and 80 wt% PEA in blends), the lower bounds increasingly become even lower, but the T_c range for formation of ring bands in the blend are similarly widened up. The same can be stated for the LM$_w$-PLLA/PTA blend, as shown in Fig. 14b; thus, discussion is abbreviated. These results can be summarized to suggest that miscibility in the PLLA/polyester blends does influence the blends' T_g, which in turn influences the lower bound and range of T_c within which the crystalline PLLA lamellae could be packed into ring-banded spherulites.

Fig. 13 POM graphs for spherulites in: **a** LM$_w$-PLLA/PEA (80/20), **b** LM$_w$-PLLA/PTA (80/20) blend melt-crystallized at T_c as indicated (110–126 °C)
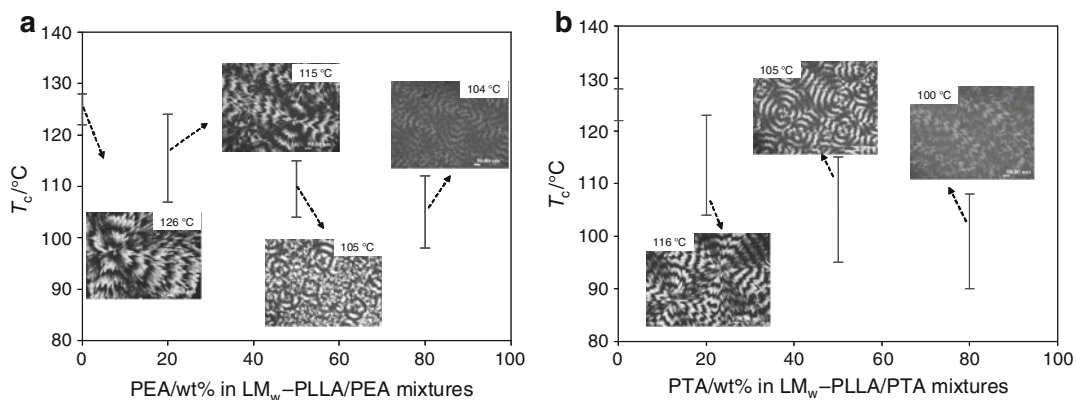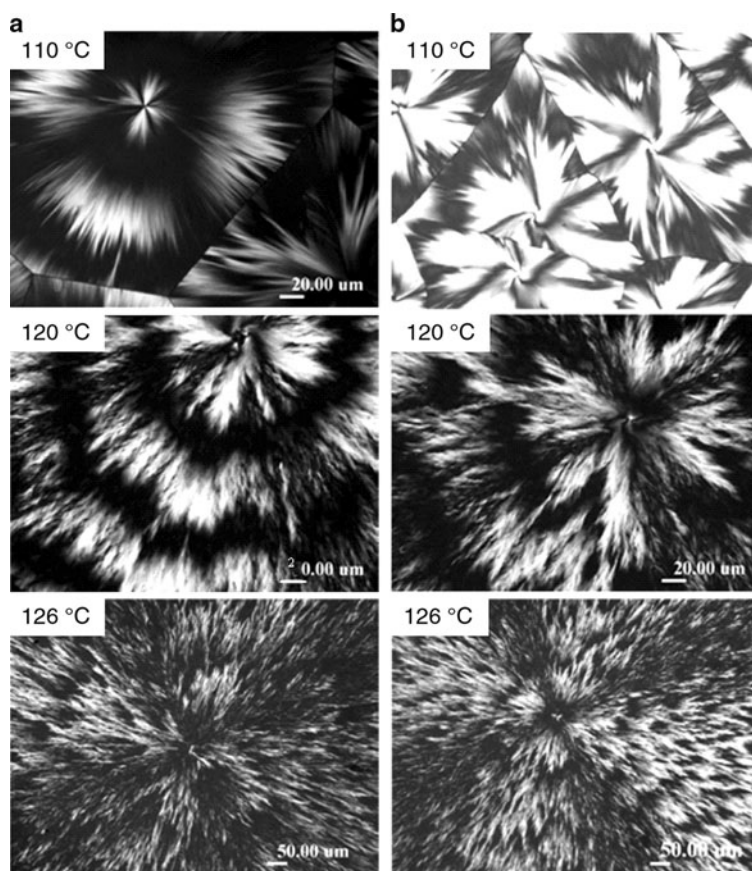

Fig. 14 Crystallization temperature range for formation of ring-banded spherulites in: **a** LM$_w$-PLLA/PEA, **b** LM$_w$-PLLA/PTA blends

Conclusions

Thermal analysis reveals that at low molecular weights of PLLA, miscibility can exist in blends of PLLA with some aliphatic polyesters. From our experiment, LM$_w$-PLLA is known to have miscibility with PEA and PTA. The chemical structures of the aliphatic polyesters apparently influence the phase behavior. The blend of LM$_w$-PLLA with PESu is a UCST system with phase transition at 220–240 °C depending on the blend composition, where

the maximum temperature of phase transition = UCST. Heating to above UCST and quick quenching was proven to preserve the UCST blend into a homogeneous glass state with a single T_g upon DSC scanning, and thermodynamic reversibility of the UCST behavior in the blend was proven by solvent recasting. High molecular weights in PLLA lead to increasingly less likely for miscibility in LMw-PLLA/polyester blends. In contrast to the LM$_w$-PLLA/PTA blend being miscible, the blend of HM$_w$-PLLA with PTA shows UCST at 195–235 °C; and the blends of HM$_w$-PLLA/PEA

and HM$_w$-PLLA/PBA are immiscible. Similarly, in contrast to the LM$_w$-PLLA/PESu blend being a UCST system (UCST = 240 °C), the blend of HM$_w$-PLLA/PESu remains to be immiscible upon heating to ~270 °C or higher. Both the molecular weights of PLLA and chemical structure of polyesters are main factors, in terms of the entropy and enthalpy contributions, respectively, which determine the phase behavior of the PLLA blends with various aliphatic polyesters.

Crystalline morphology behavior in the miscible blends of PLLA with polyesters was also examined. Neat LM$_w$-PLLA exhibits ring-banded spherulites when crystallized at the T_c range of 122–128 °C. By comparison, with increasing PEA or PTA contents in blends, the lower limit for formation of ring bands in spherulites is shifted to a lower temperature. In addition, the window range for ring-banded spherulites in LMw-PLLA/polyester blends is always wider in comparison to that for neat LMw-PLLA.

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