# Improvement in Stereocomplexation of Poly(L-lactide)/Poly(D-lactide) Blended Bioplastics by Melt Blending with Epoxidized Natural Rubber

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## Abstract

The effect of epoxidized natural rubber (ENR) blending on the stereocomplexation of poly(L-lactide) (PLL)/poly(D-lactide) (PDL) blends is evaluated. The PLL, PDL and ENR were melt blended to prepare stereocomplex polylactide (scPL) blends. The PLL/PDL ratio was fixed at 50/50 (w/w). Increasing the ENR blend ratio induced phase separation between the scPL and ENR phases of the scPL blends. The ENR blending enhanced the stereocomplexation of the scPL blends. Glass transition and crystallization temperatures of the scPL blends also decreased as the ENR blend ratio increased. The results indicated that the ENR blending had an influence on the stereocomplexation and it also gave a plasticization effect on the scPL blends.

**Keywords:** Bioplastics, Polylactide, Stereocomplex, Epoxidized natural rubber, Polymer blend

## INTROUCTION

Biodegradable bioplastics have obtained extensive attention and are considered to be a sustainable alternative to conventional oil-based plastics because of their sustainable and eco-friendly characteristics. Poly(L-lactic acid) (PLLA) or poly(L-lactide) (PLL) is a synthetic bioplastic that has been widely investigated for use in medical, pharmaceutical and packaging applications due to its biodegradability and biorenewability [1-3]. Moreover, the PLL products can be produced by conventional melt processing techniques, such as extrusion [4] and injection molding [4,5]. However, the PLL products have some problems for practical applications such as slow crystallization, high brittleness and low heat resistance [6].

In the past few decades, the blending of PLL and poly(D-lactide) (PDL) to form a stereocomplex polylactide (scPL) has been widely investigated for potential use as high performance biodegradable bioplastics [7]. The scPL shows better heat resistance, mechanical properties and hydrolysis resistance than the PLL [8-10]. The stronger van der Waals forces in the stereocomplex crystallites of scPL induced a higher melting temperature ($T_m \approx 230°C$) and faster crystallization rate than both the original PLL and PDL ($T_m \approx$

180°C) [11,12].  However, the glass transition temperature ($T_g$) of the scPL was still approximately 60°C, which was similar to the PLL.

Natural rubber (NR) has been blended with PLL for toughening PLL [13,14]. The non-polarity of NR and polarity of PLL induced high phase separation. Epoxidized NR (ENR) prepared by reacting NR with peroxide has a higher polarity than NR. The PLL/ENR blends showed better miscibility than the PLL/NR blends [15,16] because of the interactions between the epoxy groups of the ENR and the ester groups of the PLL that had occurred [17,18].

However, to the best of our knowledge, the effect of the ENR blending on the stereocomplexation and plasticization of non-chain extended and chain extended scPL has not been reported so far. Thus, the purpose of this paper was to determine the influence of the ENR blending on the phase separation and thermal transition properties of the scPL blends. The 50/50 (w/w) PLL/PDL blends with different ENR blend ratios (5 – 20 wt%) were prepared by the melt blending technique. The obtained results were also compared with the ENR-free scPL.

## EXPERIMENTAL

### Materials

L-lactide and D-lactide monomers were synthesized by direct polycondensation followed by thermal decomposition from L-lactic acid (88%, Purac, Thailand) and D-lactic acid (90%, Haihang Industry Co., Ltd., China), respectively. The crude lactide monomers were purified by re-crystallization four times from ethyl acetate before drying in a vacuum oven at 55 °C for 48 h. 1-Dodecanol (98%, Fluka, Switzerland) was 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. Epoxidized natural rubber (ENR) with a 25 mol% degree of epoxidation (Epoxyprene25®) was produced by Muang Mai Guthrie (Thailand) Co. Ltd.

## Methods

The poly(L-lactide) (PLL) and poly(D-lactide) (PDL) were synthesized by ring-opening polymerization of L-lactide and D-lactide monomers, respectively, in bulk at 165°C for 2.5 h under a nitrogen atmosphere using stannous octoate and 1-dodecanol as the initiating system. The resulting polylactides were granulated before drying in a vacuum oven at 110 °C for 3 h to remove un-reacted lactides. As determined by gel permeation chromatography (GPC), the $M_n$s of PLL and PDL were 87,500 g/mol ($M_w/M_n = 1.8$) and 52,400 g/mol ($M_w/M_n = 1.9$), respectively. The L and D enantiomer contents of the PLL and PDL obtained by the polarimetry were 96% and 97%, respectively. Melting temperatures ($T_m$) obtained by differential scanning calorimetry (DSC) were 174 and 175°C for the PLL and PDL, respectively.

The PLL, PDL and ENR were dried in a vacuum oven at 50°C for 24 h before melt blending at 200°C for 4 min using an internal mixer (HAAKE Rheomix OS lab mixers). A rotor speed of 100 rpm was chosen. The resulting scPL samples were granulated before drying in a vacuum oven at 50°C for 24 h before characterization. The PLL/PDL ratio was kept constant at 50/50 (w/w). The blends with scPL/ENR ratios of 95/5, 90/10 and 80/20 (w/w) were investigated. Neat scPL (100/0) was also prepared by the same method for comparison.

## Measurements

The chemical functional groups of the scPL were investigated using a Perkin-Elmer Spectrum GX Fourier transform infrared (FTIR) spectrometer. A resolution of 4 cm$^{-1}$ and 32 scans were employed.

The phase morphology of the scPL was investigated using a JEOL JSM-6460LV scanning electron microscope (SEM). The scPL samples were fractured after submerging in liquid nitrogen for 30 min to expose the internal morphology. The fractured samples were sputter-coated with gold to enhance the surface conductivity before scanning.

The thermal transition properties of the scPL were determined using a Perkin-Elmer Pyris Diamond differential scanning calorimeter (DSC) under a nitrogen flow. For DSC, samples (3 – 5 mg) were heated at 10 °C/min over a temperature range of 0 to 250°C for the 1st heating scan. Then, the samples were quenched to 0°C according to the DSC instrument's own default cooling mode before heating from 0 to 250°C for the 2nd heating scan. The glass transition temperature ($T_g$) was taken as the midpoint or half of the heat capacity increment associated with the glass-to-rubber transition. The crystallization ($T_c$) and melting ($T_m$) temperatures were measured as the peaks of the exothermal and endothermal phenomena in the DSC curve, respectively. The enthalpies of crystallization ($\Delta H_c$) and of melting ($\Delta H_m$) were measured from the total areas of the $T_c$ and $T_m$ peaks, respectively.

The homo-crystallinity ($X_{hc}$) and stereocomplex crystallinity ($X_{sc}$) of the scPL were determined from the melting enthalpies of the homo-crystallites ($\Delta H_{m,hc}$) and stereocomplex crystallites ($\Delta H_{m,sc}$) using equations (1) and (2), respectively.

$$X_{hc} \ (\%) = [\Delta H_{m,hc}/(w_{scPL} \times 93 \ J/g)] \times 100 \qquad (1)$$

$$X_{sc} \ (\%) = [\Delta H_{m,sc}/(w_{scPL} \times 142 \ J/g)] \times 100 \qquad (2)$$

where, $w_{scPL}$ was the weight fraction of the scPL component. The melting enthalpies for 100% crystallinities of the homo-crystallites and stereocomplex crystallites were 93 J/g and 142 J/g, respectively [19].

## RESULTS AND DISCUSSION

### FTIR

The chemical functional groups of the neat scPL and scPL/ENR blends were determined from the FTIR spectra, as shown in Figure 1. The FTIR spectra of the neat scPLs exhibited absorption band at 1743 cm$^{-1}$ attributed to the stretching vibration of the carbonyl groups (C=O) of PL [20]. From the FTIR spectrum of ENR, the absorption bands at 1449 and 1376 cm$^{-1}$ are attributed to methine (C-H) stretching from –$CH_3$ groups [20]. It can be seen that all the scPL/ENR blends exhibited both the PL and ENR characteristic bands. The wave numbers of the carbonyl bands of PL slightly increased as the ENR blend ratio increased. This suggests that some interactions between the carbonyl groups of PL and the oxirane groups of ENR had occurred [17, 18, 20].
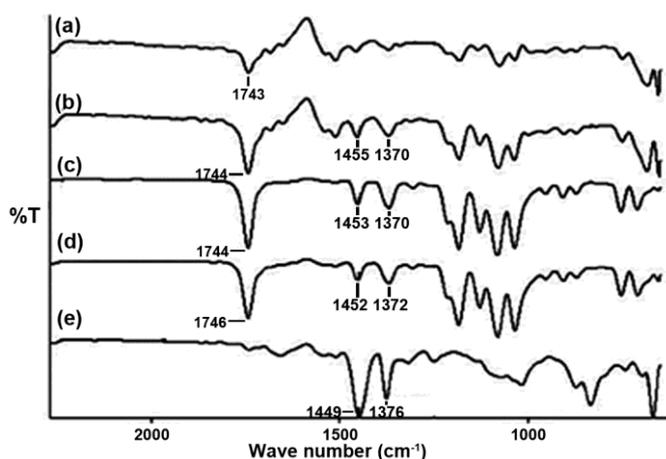


**Figure 1:** FTIR spectra of scPL blends prepared with scPL/ENR blend ratios of (a) 100/0, (b) 95/5, (c) 90/10 and (d) 80/20 wt% as well as (e) ENR.

### Phase morphology

The phase morphology of the neat scPL and scPL/ENR blends was observed from SEM images of their fractured surfaces as shown in Figure 2. The neat scPL exhibited a rough surface [Figure 2(a)]. This may be explained by a high content of stereocomplex crystallites that induced surface roughness

[21]. The fractured surfaces of the scPL/ENR blends were smoother than those of the neat scPL [Figs. 2(b) – 2(d)]. This may be due to the rubber character of the ENR that induced a smooth surface. Phase separation between the continuous scPL and dispersed ENR phases was detected for all the scPL/ENR blends. The morphology of the dispersed ENR droplets existed as internal voids on the scPL matrices. The different polarities between the PL and ENR induced phase separation [15, 16]. The sizes of the ENR droplets increased as the ENR blend ratio increased. Greater coalescence of the ENR droplets was found for the higher ENR blend ratio. The 10 and 20 wt% ENR showed larger phase separation with large amounts of elongated ENR domains [Figures 2(c) – 2(d)].
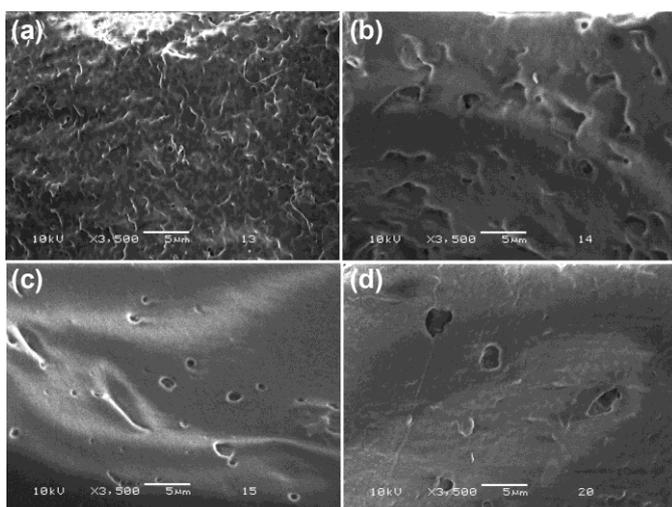


**Figure 2:** SEM images of scPL blends prepared with scPL/ENR blend ratios of (a) 100/0, (b) 95/5, (c) 90/10 and (d) 80/20 wt% (all bar scales = 5 μm).
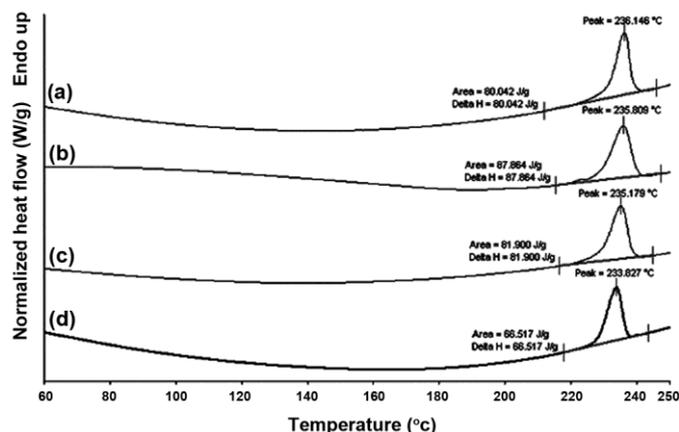


**Figure 3:** First heating scan DSC thermograms of scPL blends prepared with scPL/ENR blend ratios of (a) 100/0, (b) 95/5, (c) 90/10 and (d) 80/20 wt%.
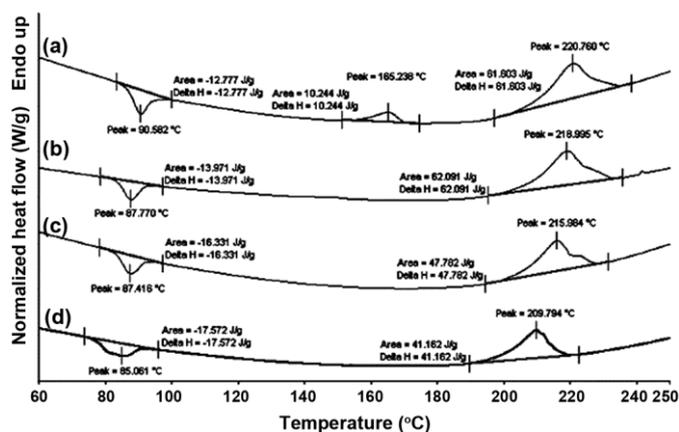


**Figure 4:** Second heating scan DSC thermograms of scPL blends prepared with scPL/ENR blend ratios of (a) 100/0, (b) 95/5, (c) 90/10 and (d) 80/20 wt%.

## Thermal transition properties

The thermal transition properties of the neat scPL and scPL/ENR blends were determined from the 1st and the 2nd heating scan DSC thermograms, as shown in Figures 3 and 4, respectively. All the neat scPL and scPL/ENR blends illustrated only a single melting peak of the stereocompex crystallites ($T_{m,sc}$) in the range 234 – 237°C from the 1st heating scan. This indicates the stereocomplexation of the neat scPL and scPL/ENR matrices was complete. The ENR blending did not induce homo-crystallization of the PL matrices. The $\Delta H_{m,sc}$ and $X_{sc}$ values of the scPL matrices are summarized in Table 1. It was found that the $X_{sc}$ values of all the scPL/ENR blends were higher than the neat scPL. This suggests the ENR blending enhanced the PL stereocomplexation. The scPL/ENR blends with 5 wt% ENR gave the highest $X_{sc}$. The $X_{sc}$ values slightly decreased when the ENR blend ratios were increased up to 10 and 20 wt%.

The $T_c$ and $\Delta H_c$ values of the blends from the 2nd heating scan (Figure 4) are reported in Table 2. The $T_c$ decreased and the $\Delta H_c$ increased as the ENR blend ratio increased. The 80/20 (w/w) scPL/ENR blends showed the fastest crystallization. Therefore, the crystallization of the PL matrices can be improved by the ENR blending. The ENR blending enhanced the rearrangement of the scPL chains for crystallization. This suggests that the ENR can act as a nucleating agent for the scPL.

In addition, from the 2nd heating scans, the neat scPLs had small melting peaks of the homo-crystallites (165°C). This indicates that the stereocomplexation of the neat scPLs was not complete from the 2n heating scans. Meanwhile, the stereocomplexation of all the scPL/ENR blends from the 2nd heating scan was complete. They had a $T_{m,sc}$ in the range 208 – 224°C. Therefore the ENR blending enhanced the stereocomplexation of the PL matrices. The $T_{m,sc}$ decreased steadily as the ENR blend ratio increased. The scPL blends

with 5 wt% ENR showed the highest $\Delta H_{m,sc}$. When the ENR blend ratios were increased, the $\Delta H_{m,sc}$ were decreased. Figure 5 shows the expanded glass transition regions of the neat scPL and scPL/ENR blends. The $T_g$ values of the blends are also summarized in Table 2. The $T_g$ decreased as the ENR blend ratio increased. This demonstrated that the blended ENR chains improved the chain mobility of the amorphous scPL matrices.

**Table 1**: Thermal transition properties of scPL/ENR blends from 1st heating scan DSC thermograms.

| scPL/ENR ratio (w/w) | $T_{m,sc}$ (°C) | $\Delta H_{m,sc}$ (J/g) | $X_{sc}^{a}$ (%) |
|---|---|---|---|
| 100/0 | 236 | 80.0 | 56.3 |
| 95/5 | 236 | 87.9 | 65.2 |
| 90/10 | 235 | 81.9 | 64.1 |
| 80/20 | 234 | 66.5 | 58.5 |

a calculated from equation (2).

**Table 2**: Thermal transition properties of scPL/ENR blends from 2nd heating scan DSC thermograms.

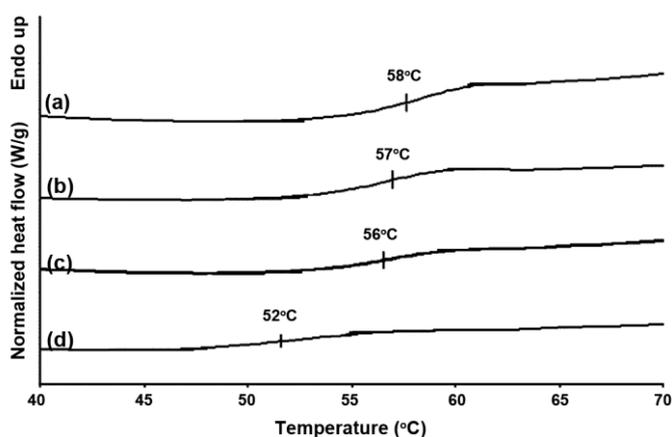| scPL/ENR ratio (w/w) | $T_g$ (°C) | $T_c$ (°C) | $\Delta H_c$ (J/g) | $T_{m,hc}$ (°C) | $T_{m,sc}$ (°C) | $\Delta H_{m,hc}$ (J/g) | $\Delta H_{m,sc}$ (J/g) |
|---|---|---|---|---|---|---|---|
| 100/0 | 58 | 91 | 12.8 | 165 | 221 | 10.2 | 61.6 |
| 95/5 | 57 | 88 | 14.0 | - | 219 | - | 62.1 |
| 90/10 | 56 | 87 | 16.3 | - | 216 | - | 47.8 |
| 80/20 | 52 | 85 | 17.6 | - | 210 | - | 41.1 |



**Figure 5:** Expanded glass transition regions from second heating scan DSC thermograms of scPL blends prepared with scPL/ENR blend ratios of (a) 100/0, (b) 95/5, (c) 90/10 and (d) 80/20 wt%.

**CONCLUSION**

In this work, the scPL/ENR blends were prepared by melt blending of the PLL, PDL and ENR. The influence of the ENR blend ratio on the phase morphology and stereocomplex formation of the scPL prepared with a 50/50 (w/w) PLL/PDL blend ratio were evaluated by FTIR, SEM and DSC. The phase separation between the scPL matrices and dispersed ENR droplets can be clearly observed as a formation of internal voids from their SEM images. The sizes of the ENR droplets increased with the ENR blend ratio. The ENR blending improved the $X_{sc}$ of the scPL matrices. The 5 wt% ENR gave the highest $X_{sc}$. The $T_g$ and $T_c$ values of the scPL blends decreased steadily as the ENR blend ratio increased. In conclusion, the ENR can act as a plasticizer and nucleating agent to enhance the stereocomplexation of the scPL matrices.

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