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**The relationship between morphology and impact toughness of
poly(L-lactic acid)/poly(ethylene oxide) blends**

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Abstract

The morphology of unannealed and annealed poly(L-lactic) acid (PLLA)/polyethylene oxide (PEO) (80/20) and (50/50) blends were studied using polarized optical microscopy (POM), scanning electron microscopy (SEM) and time-of-flight secondary ion mass spectrometry (ToF-SIMS). Samples were annealed at temperatures between 90 and 125 °C. The size of PLLA spherulites increased dramatically with annealing temperature. SEM analyses of the water-etched PLLA/PEO blend samples and ToF-SIMS analyses of the blend thin films indicated that the PEO content was higher in the interspherulitic region than in the PLLA spherulites. The distribution of PEO between the two regions (i.e. the interspherulitic region and the region of PLLA spherulites) determined the impact toughness of the unannealed and annealed PLLA/PEO blends. The unannealed PLLA/PEO (80/20) blend had the highest impact strength and very small spherulites compared to those of the annealed samples. In this case, a larger interspherulitic region, which contained a higher content of PEO, was the stronger component compared to the PLLA spherulites. For the 50/50 blends, the sample annealed at 125 °C was the strongest one because of a more even distribution of PEO content between the PLLA spherulites and the interspherulitic boundary as well as a higher PLLA crystallinity.

Key words: poly(lactic acid); poly(ethylene oxide); spherulite size; interspherulitic boundary width, Izod impact toughness.

1. Introduction

Poly(L-lactic acid) (PLLA) is a biodegradable polyester that can potentially be used in a wide range of products.^{1, 2} It can be degraded in the natural environment by the enzymatic or non-enzymatic hydrolysis of the ester bond.³⁻⁵ It is also considered as a sustainable alternative to petrochemical-derived products, since the lactides from which it is synthesized can be produced on a large scale by the microbial fermentation of carbohydrate-rich agricultural by-products.⁶ In the early years, PLLA was mainly used in bio-medical applications ranging from sutures to drug delivery system due to its low toxicity, bio-compatibility and biodegradability.^{5,7} Nowadays, it is also found in packing materials for food and consumer goods.^{8,9} PLLA has high strength and modulus.¹⁰ However, its intrinsic brittleness is always a concern and restricts its broader applications.^{11, 12} Blending PLLA with poly(butylene adipate) (PBA)¹³, poly(butylene succinate) (PBS)¹⁴, polyurethane¹⁵, and collagen¹⁶ serves to improve its mechanical performance. In addition, blending with materials with a low glass transition temperature (T_g) like poly(ϵ -caprolactone) (PCL) and poly(ethylene glycol) (PEG) can make it more ductile.¹⁷⁻²⁰ Polyethylene oxide (PEO), in particular, is an interesting low T_g material as it possesses low toxicity and good biocompatibility.²¹⁻²³ Another desirable feature of PEO is its solubility in water which makes it easy to remove.²⁴

Both PLLA and PEO are semi-crystalline polymers with very different crystallization temperatures.²⁵⁻²⁷ Reported crystallization temperatures of PLLA range from 80 to 130 °C.²⁸ At these temperatures, however, PEO is still in its molten state. The crystallization behaviors of PLLA/PEO blends are of great interest. The morphology of their blends under different annealing conditions has already been studied in recent years.²⁹⁻³¹ Water-etched annealed PLLA/PEO blend thin films were examined to determine the PEO distribution within the PLLA spherulites with more than 50 wt% of PEO.³¹ The banded structures in the spherulites of the PLLA/PEO blends were also revealed using time-of-flight secondary ion mass spectrometry (ToF-SIMS) and a profilometer.²⁹ The elongation property of PLLA was improved in the blends of PLLA and PEO.³² However, the impact toughness of PLLA/PEO blends has never been reported. The mechanical properties of PLLA/PEO blends determine their broader applications.^{32,33,42,43} It is reasonable to expect that the Izod impact toughness of PLLA is enhanced by the blending. In addition, the mechanical properties of PLLA have been

demonstrated to be significantly affected by its morphology, which is strongly controlled by the processing parameters.^{7, 33, 36, 37} Therefore, the effects of the morphology on the mechanical properties of PLLA/PEO blends deserve further investigation.

In this study, the morphology of annealed PLLA/PEO blend thin films were characterized in terms of the PLLA spherulite size and the PEO distribution in the PLLA spherulites. The Izod impact toughness of the PLLA/PEO blends with the same thermal treatments was measured to establish the relationship between the morphology and impact toughness of the blends.

2. Experimental

2.1 Materials and sample preparation

Ingeo™ 4032D with $\bar{M}_w$ of 235,000 was purchased from Natureworks, USA. This polymer contained 98.2 wt% of PLLA as determined with an optical rotator. PEO (PEO-3) with $\bar{M}_w$ of 1,020,000 was purchased from Sumitomo Seika Chemical, Japan. The melting points of the purchased PLLA and PEO were 170.1 and 65.7 °C, respectively. PLLA/PEO (80/20) and (50/50) blends with the PEO content of 20 and 50 wt%, respectively, were made using a Collin ZK 25T twin screw kneader, which has an L/D ratio of 18:1. The temperatures of the feed, transition and meter sections were 175, 205 and 165 °C, respectively. The extrudate was cooled with compressed air and then chopped into small pellets for further processing.

Solutions containing 4 wt% of the blends were prepared by dissolving the samples in chloroform and thoroughly stirring overnight. Films were prepared by casting the solutions on micro glass slides at 25 °C and were dried in a vacuum oven for 2 h. Another glass slide was placed on the top of each of these films. Then films of about 1 μm in thickness were prepared by hot-pressing the material between the two glass slides. The stage was first heated up to 210 °C for 1 min to erase the thermal history of the sample. Then the sample was cooled down to a chosen isothermal crystallization temperature at 20 °C/min. Isothermal crystallization was performed at 90, 110 and 125 °C for 3 h. Control samples were directly cooled down to 25 °C from 210 °C at 20 °C/min without annealing.

The blend pellets were dried in a vacuum oven for more than 4 h before they were transferred to the mold for hot compression molding under a force of 30 tons. The control and annealed samples for the impact tests were prepared under the same conditions as the thin films. The annealed PLLA/PEO blend sheets were cut into bars with specified dimensions (according to ASTM D256 protocol) for Izod impact tests using a Struers Secotom-1 band saw.

The arrested crack was produced from a single-edge-notched annealed impact test bar. The section containing the arrested crack was cut out and embedded in epoxy for curing. After the curing was completed, the sample was sliced using a South Bay M-650 low-speed diamond saw into thin films of around 200 μm in thickness. A green lube oil was used as the lubricant during the slicing process.

2.2 Characterization

Differential scanning calorimetry (DSC)

DSC experiments were performed on a Pyris Diamond differential scanning calorimeter (TA Q1000). To determine the crystallinity of a sample, about 0.2 mg of the sample was heated from 0 to 210°C at 10 °C/min. The thermal graph during the heating process was recorded to calculate the heat of fusion ΔH_m and the heat of crystallization ΔH_c of PLLA and PEO. The crystallinity of the polymers was determined using Equation 1:⁷

$$\text{Crystallinity}(\%) = \frac{\Delta H_m - \Delta H_c}{\Delta H_m^{100}} \times 100 \quad (1)$$

where ΔH_m^{100} is the heat of fusion for a 100% crystalline polymer. The ΔH_m^{100} for the 100% crystalline PLLA is 93.70 J/g^{20, 38} and that for 100% crystalline PEO is 205 J/g.³⁹

Polarized optical microscopy (POM)

A polarized light microscope (Olympus BX50) equipped with a Linkam CSS 450 plate and a Sony DXC-950P video camera was used to study the development of spherulites in annealed blend thin films and sections of bulk samples. Each sample was sandwiched between two microscopic slides.

Scanning electron microscopy (SEM)

Experiments were performed on several scanning electron microscopes (JEOL JSM-6390, JSM-6700F and JSM-7100F) with the accelerating voltages of 5 and 20 keV. To prevent charging, the samples for SEM analyses were sputter-coated with gold.

Time-of-flight secondary ion mass spectrometry (ToF-SIMS)

ToF-SIMS spectra and images of the surfaces of annealed PLLA/PEO (80/20) and (50/50) blend thin films were acquired using a time-of-flight secondary ion mass spectrometer (Ion-ToF

GmbH). A beam of C_{60}^{+} ions was used for sputtering and a beam of Bi_3^{+} ions at a pulse current of 0.3 pA was used as the analysis beam. The vacuum pressure was 1.5×10^{-9} Torr. Areas of 60×60 , 150×150 and $300 \times 300 \mu\text{m}^2$ (128×128 pixels) were chemically imaged at selected depths after the intensity of key ions had reached a constant value and the spectra recorded. The intensities of CH_3O^{+} ($m/z=31$) ion and $\text{C}_3\text{H}_3\text{O}^{+}$ ($m/z=55$) ion were selected to represent the concentrations of PEO and PLLA, respectively, for chemical imaging and compositional analysis.

Izod impact toughness

The annealed blend samples were kept at 23 ± 2 °C for 24 h before notching. V-shaped notches were produced by a CSI automatic notcher (CS-93M). The cutter speed and the table feed rate were about 92 and 10 cm/min, respectively. The notched samples were kept at 23 ± 2 °C for at least two weeks before the Izod impact tests were conducted.

3. Results and Discussion

Morphology of annealed blend thin films

The morphological details of the annealed and control samples were investigated using POM and the results are shown in Figure 1. At the annealing temperature of 90 °C, the spherulites were very small and had rather irregular shapes. It should be noted that the control samples of the blends (cf. Figures 1a and e) had very similar morphologies to the blends annealed at 90 °C (cf. Figures 1d and h) due to the much higher crystallization rates of PLLA in the blends at low crystallization temperatures.⁴⁰ The size of the PLLA spherulites of the blends was found to increase significantly with the annealing temperature. Banded structures were observed on large spherulites when the samples were annealed at 110 and 125 °C. These banded structures were also observed in PLLA/PEO blends with the PEO content varying from about 20 to 60 wt% at the annealing temperature of 125 °C.²⁹ The average diameters of the spherulites of the blends measured from the POM micrographs are shown in Table 1. The diameter ranged from 15 to 65 μm for the blend annealed at 90 °C, from 90 to 130 μm for the one annealed at 110 °C and from 800 to 1500 μm for the one annealed at 125 °C. The size of spherulites of neat PLLA as a function of the annealing temperature was reported in a crystallization behavior study of the polymer.⁴¹ The PLLA spherulites in the blend films annealed at 110 and 125 °C were

much larger than those of neat PLLA, which was expected because the nucleus density of PLLA in the blends was lowered by the incorporation of PEO.

Figure 1. POM micrographs of thin films: (a) the control sample of the PLLA/PEO (80/20) blend; (b), (c) and (d) the PLLA/PEO (80/20) blends annealed at 90, 110, and 125 °C, respectively; (e) the control sample of the PLLA/PEO (50/50) blend; (f), (g) and (h) the PLLA/PEO (50/50) blends annealed at 90, 110, and 125 °C, respectively.

Table 1. The sizes of PLLA spherulites in the PLLA/PEO blends annealed at different temperatures.

Blend	Annealing Temperature [°C]	Spherulite Diameter [μm]
PLLA/PEO (80/20)	Control	21.0±5.3
	90	21.9±4.2
	110	110.3±10.8
	125	921±113
PLLA/PEO (50/50)	Control	47.3±17.3
	90	47.6±15.8
	110	125.7±5.2
	125	1348±284

Distribution of components in the annealed blend thin films

Previous studies have shown that the assembly of PLLA lamellae could be revealed by washing out the PEO component of the PLLA/PEO blend thin films.^{31, 42} In the current study, the blend thin films annealed at 90 °C and 125 °C were etched with water to dissolve the PEO component. These water-etched films were examined using SEM to determine the PEO distribution. PEO is the only component that can be dissolved in water. The cracks and crevices on the surface of the water-etched blend thin films were believed to be where the PEO component was located. As shown in Figures 2a, and e (90 °C annealing) and Figures 3a and e (125 °C annealing), PEO was clearly present at the boundary separating the spherulites of the PLLA/PEO (80/20) and (50/50) blends. Figures 2b, c, and d show, respectively, the SEM micrographs of the center, middle and edge parts of a large spherulite of the PLLA/PEO(80/20) blend annealed at 125 °C. Figures 3b, c, and d show, respectively, the SEM micrographs of the center, middle and edge parts of a large spherulite of the PLLA/PEO (50/50) blend annealed at 125 °C. The micro-crevices in the large PLLA spherulites of PLLA/PEO (50/50) blend thin film annealed at 125 °C are very pronounced (cf. Figures 3f and g) whereas the PLLA/PEO (80/20) blend thin film annealed at 125 °C hardly showed any cracks or crevices (cf. Figure 2f and g). This indicates that the PEO content in the PLLA spherulites of the PLLA/PEO (80/20) blend was

not high. For the PEO/PLLA (50/50) blend samples annealed at 90 °C, the number of cracks within the PLLA spherulites was also small compared with that within the sample annealed at 125 °C. These results suggest that the PEO content in the PLLA spherulites was enhanced at a higher annealing temperature. Two studies suggested that the PEO and amorphous PLLA aggregated in the inter-lamellae regions of the PLLA spherulites.^{40, 41}

Figure 2. SEM micrographs of the water-etched PLLA/PEO (80/20) blend thin films annealed at (a) 90 °C; (b), (c), and (d) 125 °C. (e), (f), (g), and (h) the high- magnification micrographs of (a), (b), (c), and (d) respectively. The cracks and crevices are marked by the arrows.

Figure 3. SEM micrographs of the water-etched PLLA/PEO (50/50) blend thin films annealed at (a) 90 °C; (b), (c), and (d) 125 °C. (e), (f), (g), and (h) the high-magnification micrographs of (a), (b), (c), and (d) respectively. The cracks and crevices are marked by the arrows.

To quantitatively determine the spatial distribution of the blend components, ToF-SIMS analysis was performed. The sample surface was sputtered using a beam of C_{60}^{+} ions until the intensity of the characteristic ions of PLLA and PEO stayed constant to eliminate errors caused by the possible migration of a component to the surface. The characteristic CH_3O^{+} ion ($m/z=31$) and $C_3H_3O^{+}$ ion ($m/z=55$) were selected to represent PEO and PLLA, respectively. The relative intensities of these two ions were used to semi-quantify the distributions of PEO and PLLA within the selected regions. Figures 4 and 5 show the chemical images of the PLLA/PEO (80/20) and (50/50) blends, respectively. As the spherulites of the blend sample annealed at 125 °C were larger than the maximum scanning area of $500 \times 500 \mu m^2$, selected regions on a large spherulite were analyzed. Banded structures can be observed due to the regular variation in PEO and PLLA concentrations across the thin films. Boundaries separating the spherulites can be identified by the regions showing high PEO contents.

Figure 4. $\text{C}_3\text{H}_3\text{O}^+$ ($m/z=55$) and CH_3O^+ ($m/z=31$) ion images of the C_{60}^+ -sputtered surface of PLLA/PEO (80/20) blend thin films annealed at 90 and 125 °C.

Figure 5. $\text{C}_3\text{H}_3\text{O}^+$ ($m/z=55$) and CH_3O^+ ($m/z=31$) ion images of the C_{60}^+ -sputtered surface of PLLA/PEO (50/50) blend thin films annealed at 90 and 125 °C.

The relative intensities of the CH_3O^+ ($m/z=31$) ion, $I_{\text{CH}_3\text{O}^+}$, and the $\text{C}_3\text{H}_3\text{O}^+$ ($m/z=55$) ion, $I_{\text{C}_3\text{H}_3\text{O}^+}$, of the spherulites and interspherulitic boundary of the blends are shown in Figures

6 and 7, respectively. As shown in Figure 6, $I_{\text{CH}_3\text{O}^+}$, which can be used as a measure of the PEO concentration, increased significantly when the PEO content increased from 25 to 50 wt%, especially at the boundary between the PLLA spherulites. This result confirmed that PEO tended to aggregate to the interspherulitic region. Assuming that the PEO concentration was roughly proportional to $I_{\text{CH}_3\text{O}^+}$, we could then estimate the PEO content in the different regions of the blend films. To assist data analysis, we defined three ratios:

$$R_s = \frac{I_{\text{PEO}}^s(125^\circ\text{C})}{I_{\text{PEO}}^s(90^\circ\text{C})} \quad (2)$$

where $I_{\text{PEO}}^s(125^\circ\text{C})$ is $I_{\text{CH}_3\text{O}^+}$ of the spherulites of a blend annealed at 125 °C and $I_{\text{PEO}}^s(90^\circ\text{C})$ is $I_{\text{CH}_3\text{O}^+}$ of the spherulites of a blend annealed at 90 °C;

$$R_i = \frac{I_{\text{PEO}}^i(125^\circ\text{C})}{I_{\text{PEO}}^i(90^\circ\text{C})} \quad (3)$$

where $I_{\text{PEO}}^i(125^\circ\text{C})$ is $I_{\text{CH}_3\text{O}^+}$ of the interspherulitic boundary of a blend annealed at 125 °C and $I_{\text{PEO}}^i(90^\circ\text{C})$ is $I_{\text{CH}_3\text{O}^+}$ of the interspherulitic boundary of a blend annealed at 90 °C; and

$$R_{i/s} = \frac{I_{\text{PEO}}^i(T)}{I_{\text{PEO}}^s(T)} \quad (4)$$

where $I_{\text{PEO}}^s(T)$ and $I_{\text{PEO}}^i(T)$ are $I_{\text{CH}_3\text{O}^+}$ of the spherulites and $I_{\text{CH}_3\text{O}^+}$ of the interspherulitic boundary of a blend annealed at T , respectively.

Table 2 shows a summary of the calculated values of these ratios for these two blends. Notice that R_s and R_i of both the PLLA/PEO (50/50) and (80/20) blends were larger than one, suggesting that more PEO was redistributed to the PLLA spherulites and the interspherulitic region after annealing at 125 °C. This redistribution of the PEO to the spherulites and the interspherulitic region was caused by a reduction in the size of the high-PEO-content interspherulitic region after the annealing due in turn to a dramatic increase in the spherulite size.

For the PLLA/OEO (50/50) blend, $R_{I/S}(90^{\circ}\text{C})$ was larger than $R_{I/S}(125^{\circ}\text{C})$ suggesting a more even distribution of PEO between the PLLA spherulites and the interspherulitic region after annealing at a higher temperature. However, for the PLLA/PEO (80/20), $R_{I/S}(90^{\circ}\text{C})$ was smaller than $R_{I/S}(125^{\circ}\text{C})$ suggesting a stronger segregation of the PEO to the interspherulitic region. In addition, the widths of the boundaries were determined from the $\text{C}_3\text{H}_3\text{O}^+$ ($m/z=55$) and CH_3O^+ ($m/z=31$) ion images and the results are shown in Figure 8. The increase in PEO concentration in the interspherulitic region and the PLLA spherulites as well as the width of the boundary after annealing could have a substantial effect on the impact toughness of the blends.

Figure 6. The relative ion intensity of CH_3O^+ ($m/z=31$) measured from the PLLA spherulites and interspherulitic region of the (a) PLLA/PEO (80/20) and (b) PLLA/PEO (50/50) blend thin films annealed at 90°C and 125°C .

Figure 7. The relative ion intensity of $C_3H_3O^+$ ($m/z=55$) measured from the PLLA spherulites and interspherulitic region of the (a) PLLA/PEO (80/20) and (b) PLLA/PEO (80/20) blend thin films annealed at 90 °C and 125 °C.

Table 2. A summary of the calculated values of R_s , R_l and $R_{l/s}(T)$ for the annealed PLLA/PEO blends.

Sample	R_s	R_l	$R_{l/s}(90^\circ C)$	$R_{l/s}(125^\circ C)$
PLLA/PEO(80/20)	1.11	1.21	1.74	1.80
PLLA/PEO(50/50)	1.27	1.13	1.58	1.37

Figure 8. The width of the interspherulitic boundary of the PLLA/PEO (80/20) and (50/50) blends annealed at 90 °C and 125 °C.

3.2 Impact toughness

The impact toughness results of the control and annealed samples are summarized in Table 3 and shown in Figure 9. For the neat PLLA, the sample annealed at 90 °C had the highest impact strength due to the small spherulite size and higher crystallinity. A comparison between the neat PLLA and blend samples indicates that the impact toughness was significantly increased when PLLA was blended with PEO. The impact toughness of PLLA/PEO (50/50), increased

from $8.9 \pm 0.9 \text{ kJ/m}^2$ to $27.6 \pm 2.8 \text{ kJ/m}^2$ after annealing at 125°C . However, the situation for the PLLA/PEO (80/20) blend was quite different. The results shown in Table 3 suggest that the impact strength was the highest for the PLLA/PEO (80/20) blend without annealing. These two blends presented a very interesting case showing the opposite effects of annealing on the impact strength of blends.

Table 3. The impact toughness and crystallinity of the control and annealed neat PLLA as well as control and annealed PLLA/PEO blend samples. The samples were annealed at selected temperatures for 3 h.

Sample	Annealed temperature [$^\circ\text{C}$]	Crystallinity [%]		Impact toughness [kJ/m^2]
		PLLA	PEO	
PLLA	Control	2.6	-	2.8 ± 0.2
	90	36.3	-	3.9 ± 0.3
	125	46.2	-	3.5 ± 0.3
PLLA/PEO (80/20) blend	Control	43.1	39.9	11.9 ± 2.7
	90	46.3	41.8	9.9 ± 1.1
	110	-	-	9.1 ± 0.6
	125	54.2	45.8	5.6 ± 0.9
PLLA/PEO (50/50) blend	Control	50.9	62.8	10.2 ± 0.9
	90	51.1	63.1	11.9 ± 0.5
	110	-	-	20.5 ± 1.3
	125	61.5	64.9	27.6 ± 2.8

Figure 9. The impact toughness of the control and annealed PLLA as well as control and annealed PLLA/PEO (80/20) and (50/50) blends.

Fracture surface analysis

Figure 10 shows SEM micrographs of the fracture surfaces near the notch root of the control and annealed PLLA samples. Parallel bands appeared on the fracture surface of the control PLLA sample (cf. Figures 10a and d). These parallel bands consisted of the stretched-out fibrils as shown in the high-magnification micrograph in Figure 10d. Te-like patterns, which were created on the fracture surfaces of the samples annealed at 90 and 125 °C (cf. Figure 10b and c), were induced by the fracturing of the PLLA spherulites in the annealed sample. Their size increased as annealing temperature increased. The fracture surfaces of the annealed samples, which were much rougher than that of the control, showed more elongated thin fibrils.

Figure 10. SEM micrographs of the fracture surface of the control and annealed PLLA samples. The upper row and lower row are micrographs with 50x and 3000x magnification, respectively. (a) and (d) the PLLA control sample; (b) and (e) the PLLA sample annealed at 90 °C; (c) and (f) the PLLA sample annealed at 125 °C. The direction of propagation of fractures is indicated by the arrow.

The SEM micrographs of the fracture surface near the notch root of the annealed PLLA/PEO (80/20) and (50/50) blend samples are shown in Figure 11. Concentric circles are observed on the fractured surface of the PLLA/PEO (80/20) blend sample annealed at 125°C, as shown in Figure 11c. A few smaller concentric circular patterns can also be seen on the fractured surface of the PLLA/PEO (80/20) blend annealed at 110°C, as shown in Figure 11b. These features were caused by the fracturing of the spherulites of the annealed blend samples which had visible banded structures as shown in the POM micrographs (c.f. Figure 1). For the PLLA (80/20) sample annealed at 90°C, only tiny PLLA te-like patches can be observed on the surface. This difference was possibly due to the rather small size of the PLLA spherulites of this sample. For the PLLA/PEO (50/50) blend samples, the size of these te-like patterns and the degree of local deformation on the fractured surfaces were observed to increase after annealing at a higher temperature. Figure 12 shows high-magnification SEM micrographs of the fracture surfaces of these annealed blends. The PLLA/PEO (80/20) blend sample did not show much

plastic deformation on the surface and the relatively smooth fracture surfaces suggested that the impact toughness was not very high. But the fibril density on the fracture surface of the PLLA/PEO (80/20) blend sample annealed at 90 °C was much higher than that of the same blend sample annealed at 125 °C, supporting the results that the former sample had a higher impact toughness. These fibrils generated during the fracturing process can retard the crack propagation while absorbing energy during the fracturing process (cf. Figures 12a and b). Thus the PLLA/PEO (80/20) blend annealed at 90 °C exhibited a higher impact toughness than that annealed at 125 °C. Few fine and elongated fibrils were detected on the surface of the annealed PLLA/PEO (50/50) blends but PLLA plastic deformation was prevalent on their fractured surfaces, as shown in Figures 11c and d. The fracture surface of the PLA/PEO (50/50) blend sample annealed at 125 °C was stretched to a higher degree than the sample annealed at 90 °C, as shown in Figures 11c and d.

Figure 11. Low-magnification SEM micrographs of fracture surface of the PLLA/PEO (80/20) blend samples annealed at (a) 90 °C , (b) 110 °C and (c) 125 °C as well as PLLA/PEO (50/50) blend samples annealed at (d) 90 °C , (e) 110 °C and (f) 125 °C. The direction of propagation of fractures is indicated by the arrows.

Figure 12. High-magnification SEM micrographs of the fracture surface near the notch root of the annealed blend samples. (a) and (b) the PLLA/PEO (80/20) blend samples annealed at 90 and 125 °C, respectively; (c) and (d) the PLLA/PEO (50/50) blend samples annealed at 90 and 125 °C, respectively. The direction of propagation of fractures is indicated by the arrows. The scale bar represents 5μm.

Locus of failure

To understand why annealing had such a strong effect on the impact strength of the blends requires full knowledge of the effects of annealing on the morphology and the locus of failure of these samples. To determine the locus of failure, thin sections of annealed impact bars containing an arrested crack was examined using POM and the results are shown in Figure 13. The crack obviously passed through the PLLA spherulites of both PLLA/PEO (80/20) and (50/50) blends annealed at 125 °C. For samples containing small spherulites (control and samples annealed at 90 °C), the images were quite blurred due to smearing caused by the sectioning process. The samples shown in Figure 13 had the lowest and highest impact toughness. It is reasonable to assume that the loci of failure were the same for the PLLA/PEO

(80/20) and (50/50) blends annealed at both 90 °C and 125 °C because the PEO content for all annealed samples was the highest at the interspherulitic region of the samples, implying failure along the interspherulitic boundary was highly unlikely.

Figure 13. POM micrographs showing the locus of failure in (a) the PLLA/PEO (80/20) blend annealed at 125 °C and (b) the PLLA/PEO (50/50) blend annealed at 125 °C. The scale bar represents 200µm.

Effects of annealing

As discussed in the previous section, the size of the PLLA spherulites of the blends increased with annealing temperature and the control samples had the smallest PLLA spherulites. The spherulites of the PLLA/PEO (80/20) and (50/5) blends increased in size by about 40 and 30 times, respectively, after annealing at 125 °C (cf. Table 1). Thus, the size of PLLA spherulites and the size of the interspherulitic region were the major differences between the unannealed and annealed blend samples. For the PLLA/PEO (80/20) blends, the impact toughness decreased with increasing PLLA spherulite size. One of the critical effects of increasing the PLLA spherulite size was the reduction in the size of the interspherulitic region. Figure 9 illustrates the effects of annealing on the impact strength of these two blends. The strongest PLLA/PEO (80/20) blend sample was the one without annealing. This sample had very small spherulites and hence a large volume of interspherulitic region. On the contrary, the strongest PLL/PEO (50/50) blend sample was the one annealed at 125 °C. This sample had very large spherulites and hence a smaller interspherulitic region. Based on the POM micrographs shown in Figure 13, the loci of failure

for the strongest and weakest samples were the same. Thus the size of the spherulites, the size of the interspherulitic region and the PEO concentration were likely the major factors controlling the impact toughness. In particular, the change in the concentration of the PEO in the interspherulitic region and the spherulites upon annealing likely played the most vital role. For the strength of spherulites, the controlling factors were the PEO content and the crystallinity, while the PEO content and the boundary width determined the strength of the interspherulitic region. The strongest PLLA/PEO (80/20) blend was the control (the one without annealing), which had very small spherulites and a large size of interspherulitic region.

As mentioned before, the morphology and impact strength of the control and the PPLA (80/20) blends annealed at 90 °C were similar. Thus, we would treat the values of $R_{I/S}(90^{\circ}\text{C})$ for the control and unannealed PLLA/PEO (80/20) blends as very similar. $R_{I/S}(90^{\circ}\text{C})$ of the control was then assumed to be around 1.74, which is the highest among all blends. With a large size of the interspherulitic region and a high value of $R_{I/S}(90^{\circ}\text{C})$, the distribution of PEO in this blend was most likely concentrated in the interspherulitic region instead of the spherulites. As a result, the interspherulitic region should be much stronger than the spherulites and should bear most of the load during impact. The weakest PLLA/PEO (80/20) blend was the one annealed at 125 °C, which had large spherulites. In addition, the PLLA spherulitic region was much larger than interspherulitic region. With $R_S=1.11$, the concentration of PEO in the PLLA spherulites of this blend did not increase to any significant extent after annealing at 125 °C. Therefore, the spherulitic region was expected to be much weaker than the interspherulitic region. Therefore, the control PLLA/PEO (80/20) blend was the strongest simply because the failure path had to pass through many strong interspherulitic boundaries.

The strongest PLLA/PEO (50/50) sample, was the one annealed at 125 °C. $R_{I/S}(T)$ of this blend decreased from 1.58 to 1.37 when the annealing temperature increased from 90 to 125 °C. This result suggests that more PEO was redistributed to the PLLA spherulites than to the interspherulitic region upon annealing at 125 °C. As a result, the concentration of PEO in the PLLA spherulites would not be much lower than that in the interspherulitic region. Therefore, the strength of the spherulites should be higher due to a higher PEO content and a higher crystallinity (61.5%) and is possibly comparable to that of the interspherulitic region. For the

blend annealed at 90 °C (assuming its morphology was similar to that of the control sample), the combination of a larger interspherulitic region with a high PEO content and weaker spherulites with a low PEO content and a lower crystallinity (51.1%) made it less strong than the blend annealed at 125 °C which had both strong PLLA spherulites and a large interspherulitic region.

4. Conclusions

The size of PLLA spherulites increased dramatically with annealing temperature in PLLA/PEO (80/20) and (50/50) blends. The results of ToF-SIMS analyses revealed that PEO tended to aggregate to the interspherulitic region. A high PEO content was found in the larger spherulites which were formed in the blend thin films annealed at 125 °C, especially in the spherulites of the PLLA/PEO (50/50) blends. The toughness of PLLA, which was largely improved by the blending with PEO, was shown to be closely related to the morphology of the blends and the PEO distribution between the interspherulitic region and the PLLA spherulites. Annealing of the PLLA/PEO (80/20) and (50/50) blends produced opposite effects on their impact toughness. For the neat PLLA and PLLA/PEO (80/20) blends, their impact toughness decreased after annealing because of the significant reduction in the size of the interspherulitic region (the stronger component of the blend) and a large increase in the size of PLLA spherulites (the weaker component of the blend). For the PLLA/PEO (50/50) blend sample, its impact toughness was improved after annealing at 125 °C because of a more even redistribution of the PEO between the interspherulitic region and the large PLLA spherulites.

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