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Author(s)	Sun, Guoxing; Chan, Chi-Ming; Weng, Lu-Tao; Schultz, Jerold M.
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FORMATION OF BANDED AND NON-BANDED POLY(L-LACTIC ACID) SPHERULITES DURING CRYSTALLIZATION OF FILMS OF POLY(L-LACTIC ACID)/POLY(ETHYLENE OXIDE) BLENDS

Guoxing Sun¹, Chi-Ming Chan^{1,2*}, Lu-Tao Weng³, and Jerold M. Schultz⁴

¹ Department of Chemical and Biomolecular Engineering – kesun@ust.hk; kecmchan@ust.hk

² Division of Environment – kecmchan@ust.hk

³ Materials Characterization and Preparation Facility – mcltweng@ust.hk

The Hong Kong University of Science and Technology, Clear Water Bay, Hong Kong.

⁴ Department of Chemical Engineering, University of Delaware, Newark, Delaware 19716, USA – schultz@udel.edu

Abstract - In this study, a series of poly(L-lactic acid) (PLLA)/poly(ethylene oxide) (PEO) blends with different PLLA concentrations was prepared. Films of these blends crystallized with and without a top cover were characterized by the presence and absence of banded structures, respectively. This difference in morphology was due to the oxidation of PEO during the crystallization of the blends without a cover and migration of PEO to the interface when a cover was used.

Keywords: poly(L-lactic acid); poly(ethylene oxide); banded spherulites, XPS, ToF-SIMS.

Introduction

PLLA as a biomaterial has many applications.¹ PEO is a highly biocompatible, and pharmacologically inactive water-soluble polymer.² For the past two decades, polymer scientists have been eagerly blending PLLA and PEO to take advantage of their complementary properties. Non-banded spherulites were observed in pure PLLA and pure PEO³, whereas banded spherulites were observed in their binary mixtures due to lamellar twisting⁴⁻⁹. Though the crystallization and morphology of PLLA/PEO blends are influenced by many complicated factors, two such factors, which have received very little attention, are the oxidation of PEO and the interface between the sample and the substrate. In this study, we investigated the effects of PEO oxidization and the influence of the interface on the morphology in PLLA/PEO blends.

Experimental

PLLA was obtained from Zhejiang Hisun Biomaterials Co. Ltd. Its weight-average molecular weight was 120,000 g/mol. PEO was obtained from Aldrich Chemical Co. Inc. Its viscosity-average molecular weight was 600,000 g/mol. Films of pure PLLA and pure PEO, and PLLA/PEO blends were prepared by casting chloroform polymer solutions onto glass slides, silicon wafers and Kapton films. A blend with 50 wt% PLLA and 50 wt% PEO is denoted by PLLA/PEO (50/50). The thicknesses of the films were measured using a profilometer. All samples were examined using time-of-flight secondary ion mass spectrometry (ToF-SIMS), X-ray photoelectrons spectroscopy (XPS) and polarizing optical microscopy (POM) techniques after successfully removing the coverslip if a coverslip was used.

Results and Discussion

Figure 1 shows a POM micrograph of a film of the PLLA/PEO (50/50) blend crystallized on a glass slide at 125 °C for five hours. Large non-banded spherulites are seen in the uncovered area (to the left of the yellow line in Figure 1), while banded spherulites can be observed in the covered area (to the right of the yellow line in Figure 1).

Figure 1. A polarizing optical micrograph of spherulites that formed in a 3-μm-thick film of a PLLA/PEO (50/50) blend crystallized at 125 °C for five hours on a glass slide. The right half of the sample was placed under a glass coverslip.

To investigate the effects of a coverslip on the morphology of the PLLA/PEO blends, ToF-SIMS was used to determine the surface chemical composition of the polymer blend films prepared with and without a coverslip. The peak area ratios of characteristic ions of PLLA to that of PEO were calculated. $C_3H_4O^+$ to $C_3H_7O^+$, $C_3H_4O^+$ to $C_2H_4O^+$ and $C_3H_3O^+$ to $C_3H_7O^+$ were used to indicate the concentration ratio of PLLA to PEO. The results show that the PLLA-to-PEO ratio on the surface of the film crystallized without a coverslip was much higher than that on the surface of the film crystallized under a glass coverslip or a Kapton film as the coverslip.

A relevant experiment was performed by annealing pure PEO films at 125°C for 30 minutes in the air. Pure PEO only has one peak, at 532.2eV,

corresponding to the O atoms of the C-O-C group. The XPS spectrum of an annealed PEO film indicates that the O 1s peak shifted to a higher binding energy, indicating that oxidation of PEO did occur at high temperature.

The XPS results show that the surfaces of the PLLA/PEO (50/50) blends crystallized at 125 °C for five hours without a coverslip in nitrogen contained more than 96 wt% PLLA. For the blend prepared with a glass coverslip under the same crystallization conditions, the surface contained 50 wt% PLLA and 50 wt% PEO; for the blend prepared with a Kapton coverslip, the surface contained 53 wt% PLLA and 47 wt% PEO. These results, which are consistent with the ToF-SIMS results, strongly suggest that the low surface energy component (i.e., PLLA) is significantly less driven to migrate to the interface between the coverslip and the blend than it is to migrate to the free surface of the blend.

The surface tensions of PLLA, original and oxidized PEO, glass and Kapton were measured using the contact angle method and calculated using the geometric-mean equation. The values are shown in Table 1. The interfacial tensions between PLLA and the glass slide (or the Kapton film) and between PEO and the glass slide (or the Kapton film) are shown in Table 2. These results reveal the reason that PLLA segregates to the surface and to the interface to very different extents.

Table 1. Surface tensions of PLLA, PEO, glass and Kapton at room temperature.

Material		Surface tension (mJ/m ²)		
		Dispersion	Polar	Total
PLLA	amorphous	11.8±0.7	18.9±0.7	30.7±0.1
	flat-on lamellae	4.6±0.5	53.5±2.5	58.1±2.0
	edge-on lamellae	11.4±0.7	21.2±0.9	32.6±0.6
Amorphous PEO		8.2±0.5	32.1±1.2	40.3±0.9
Glass		22.1±0.7	46.2±0.5	68.3±1.2
Kapton		7.2±0.9	38.6±0.7	45.8±0.9

Table 2. Interfacial tensions between the polymer and the substrate.

Material		Interface tension (mJ/m ²)	
		Glass	Kapton
PLLA	Amorphous	7.6±0.1	4.0±0.4
	flat-on lamellae	6.9±0.8	1.5±0.5
	edge-on lamellae	6.6±0.3	3.1±0.4
Amorphous PEO		4.7±0.2	0.4±0.2

In order to determine if the oxidation of PEO in fact could influence the morphology, POM was employed to characterize a film of the PLLA/PEO (50/50) blend crystallized at 125 °C for five hours without a coverslip

under nitrogen protection. The thickness of the film was measured to be 3 µm. Though the surface still consisted mostly of PLLA, clear banded spherulites could be observed (c.f., Figure 2). This result demonstrates that the non-banded structure shown in Figure 1 was caused by the oxidation of PEO during annealing in air.

Figure 2. A polarizing optical micrograph of spherulites that formed in a 3-µm-thick film of a PLLA/PEO (50/50) blend crystallized at 125 °C for five hours on a glass slide under a nitrogen atmosphere.

Conclusions

This work has shown that the oxidation of PEO in PLLA/PEO blends inhibits the formation of banded spherulites. The oxidation of PEO, and the surface segregation of PLLA, could however be prevented by crystallization under a coverslip. This work has also revealed that the surface chemical composition of banded spherulites formed between a coverslip and a substrate is associated with the periodic change in the surface morphology of the PLLA component.

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