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Crystallization and phase separation in blends of high stereoregular poly(lactide) with poly(ethylene glycol)

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Abstract

The effect of cooling rate on crystallization and subsequent aging of high stereoregular poly(lactide) (PLA) blended with poly(ethylene glycol) (PEG) was studied by thermal analysis and by direct observation of the solid state structure with atomic force microscopy (AFM). Blending with PEG accelerated crystallization of PLA. When a PLA/PEG 70/30 (wt/wt) blend was slowly cooled from the melt, PLA crystallized first as large spherulites followed by crystallization of PEG. The extent of PLA crystallization depended on the cooling rate, however, for a given blend composition the PEG crystallinity was proportional to PLA crystallinity. The partially crystallized blend obtained with a cooling rate of 30 °C min^{-1} consisted of large spherulites dispersed in a homogeneous matrix. The blend was not stable at ambient temperature. With time, epitaxial crystallization of PEG on the edges of the spherulites depleted the surrounding region of PEG, which created a vitrified region surrounding the spherulites. Further from the spherulites, the homogeneous amorphous phase underwent phase separation with formation of a more rigid PLA-rich phase and a less-rigid PEG-rich phase. Decreasing the amount of PEG in the blend decreased the crystallization rate of PLA and increased the nucleation density. The amount of PLA crystallinity did not depend on blend composition, however, PEG crystallinity decreased to the extent that PEG did not crystallize in a PLA/PEG 90/10 (wt/wt) blend.

Keywords: Poly(lactide); Poly(lactide)/poly(ethylene glycol) blends; Aging

1. Introduction

The tendency for poly(lactide) (PLA) plasticized with poly(ethylene glycol) (PEG) to lose properties with time at ambient temperature is a major obstacle to its application as a biodegradable packaging material. Without plasticizer, PLA is stiff and brittle. Blending with low molecular weight PEG improves elongation at break and softness [1–6]. The desired mechanical properties are achieved in quenched PLA/PEG blends with 30 wt% PEG. However, the blends are not stable at ambient temperature and the attractive mechanical properties are lost over time. Crystallization and phase separation are possible aging processes [5,6].

We previously studied aging of homogeneous amorphous PLA/PEG blends that were obtained by quenching from the melt. The kinetics and mechanism of ambient temperature aging strongly depended on stereoregularity of PLA. Lower stereoregular PLA appeared to be miscible with 30 wt% PEG at ambient temperature. Stiffening was caused by slow crystallization of PEG from the homogeneous matrix [5]. As aging gradually depleted the amorphous matrix of PEG, the glass transition increased; aging ceased when the glass transition temperature reached ambient temperature. Blends of higher stereoregular PLA with 30 wt% PEG phase-separated at ambient temperature before either constituent crystallized [6]. As formation of a PEG-rich phase depleted the matrix of PEG, the matrix became stiffer.

Higher stereoregular PLA readily crystallizes from blends with PEG if the blend is slowly cooled from the melt. Blending with PEG reportedly decreases the nucleation density but increases spherulite growth rate of PLA [3]. The PEG constituent also crystallizes under these conditions, but does not cocrystallize with PLA [7]. We have extended our previous studies of quenched blends to consider the effect of crystallinity on the ambient temperature aging of higher stereoregular PLA blended with PEG.

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We have varied the cooling rate from the melt in order to vary the amount of PLA crystallinity. Changes in solid state structure during subsequent ambient temperature aging are compared with previous observations on quenched amorphous blends.

2. Experimental

2.1. Materials

Poly(ethylene glycol) (PEG) with molecular weight 8000 and a poly(lactic acid) (PLA) with D-lactide content of 5%, $M_w = 190$ kDa, and $M_w/M_n = 1.5$ were described previously [6]. The PLA exhibited 40% crystallinity after annealing at 100 °C for 1000 min with melting temperature 151 °C, which was consistent with this D-lactide content [8]. The PEG was highly crystalline, even after quenching the crystallinity was about 95% with melting temperature of 63 °C.

2.2. Methods

The polymers were vacuum dried overnight at 50 °C before processing. Melt-blends with compositions PLA/PEG 90/10, 80/20 and 70/30 wt/wt were prepared using a counter-rotating twin screw extruder operating at 190 °C.

Differential scanning calorimentry (DSC) was carried out with a Perkin Elmer DSC-7. Specimens weighing 5–10 mg were heated at 185 °C for 4 min in the DSC, cooled to −50 °C at various cooling rates, and heated to 185 °C at 10 °C min^{-1}. The cooling thermograms were normalized to 10 °C min^{-1} to facilitate comparison. Specimens identified as quenched were cooled at 100 °C min^{-1} in the DSC.

For the aging study, larger specimens were heated at 185 °C for 4 min in the DSC, cooled to −50 °C at 30 °C min^{-1}, and aged for various periods of time at ambient conditions. Thermograms of aged specimens were obtained with a heating rate of 10 °C min^{-1}. Percent crystallinity was calculated from the melting or crystallization enthalpy using heats of fusion of 197 J g^{-1} for PEG [9] and 94 J g^{-1} for PLA [8]. The reported crystallinity is normalized to the weight fraction of the constituent in the blend.

Atomic force microscopy (AFM) was performed on surfaces microtomed at ambient temperature (Ultramicrotome MT6000-XL from RMC, Tucson, AZ) or on free melt surfaces. The morphology was too sensitive to water condensation to microtome at cryogenic temperatures. Specimens were imaged with a Nanoscope IIIa with MultiMode head and J-scanner. The tapping mode was used at ambient conditions. Commercial Si probes were chosen with a resonance frequency in the 300 kHz range. Height and phase images were recorded simultaneously.

Thin sections were microtomed at ambient temperature from DSC samples, placed between glass slides, and examined with transmission polarized light microscopy. A hot stage was used to examine specimens at elevated temperatures.

3. Results and discussion

3.1. Crystallization of PLA/PEG 70/30 during cooling

Thermograms of quenched PLA and PLA/PEG blends are shown in Fig. 1. Quenched PLA was amorphous and did not cold-crystallize upon heating at 10 °C min^{-1}. The PLA/PEG blends were also amorphous when quenched. They exhibited a glass transition that shifted to lower temperature as the PEG content increased. The T_g decreased from 60 °C for quenched PLA through ambient temperature to 12 °C for the PLA/PEG 70/30 blend. When the blends were heated at 10 °C min^{-1}, PLA cold-crystallized at about 85 °C. The cold-crystallization temperature of PLA decreased slightly as the PEG content increased in parallel with the shift in T_g. The subsequent melting temperature and amount of crystallinity relative to PLA in the blend were essentially constant for the different blend compositions. Quenched PEG was highly crystalline; it achieved 95% crystallinity with melting temperature of 63 °C. However, PEG did not crystallize in the blends during quenching or during subsequent heating.

Thermograms of PLA/PEG 70/30 with different cooling rates are shown in Fig. 2a. If the cooling rate was 30 °C min^{-1} or less, PLA crystallized during cooling, followed by crystallization of PEG at a lower temperature. Crystallization enthalpy and crystallization temperature of PLA and PEG increased as the cooling rate decreased. The effect of cooling rate on the subsequent heating thermogram is shown in Fig. 2b. As the cooling rate decreased, an

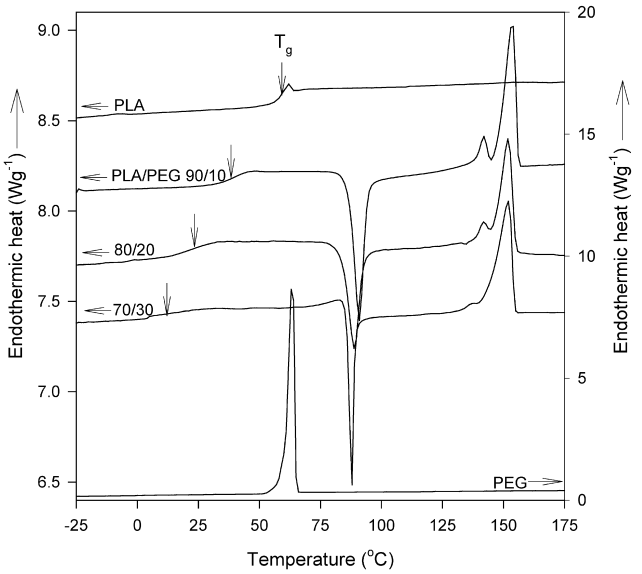

Fig. 1. Thermograms of quenched PLA/PEG blends obtained with a heating rate of 10 °C min^{-1}.

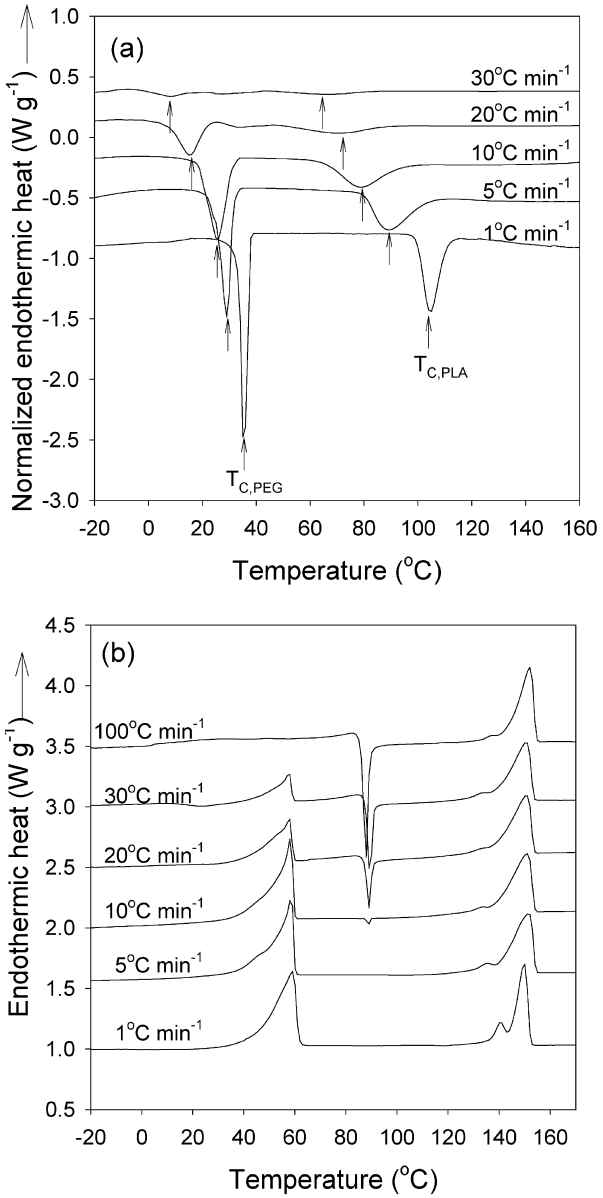

Fig. 2. Effect of cooling rate on crystallization and melting thermograms of PLA/PEG 70/30: (a) cooling thermograms obtained with the cooling rate indicated; and (b) subsequent heating thermograms obtained with a heating rate of 10 °C min^{-1}.

endothermic peak corresponding to melting of PEG appeared at about 55 °C in the heating thermogram. The melting enthalpy corresponded to the crystallization enthalpy in the cooling thermogram. Also, as the cooling rate decreased from 100 to 10 °C min^{-1}, the cold-crystallization peak of PLA decreased until it disappeared entirely when the cooling rate was 5 °C min^{-1} or less. The subsequent melting temperature and melting enthalpy of PLA were not affected by the cooling rate. The double melting peak of PLA, which has been attributed to lamellar reorganization [1,4], became more pronounced at lower cooling rates.

Qualitatively, it appeared that if the cooling rate was slow enough, PLA was able to crystallize during cooling. Slower cooling increased the amount of PLA crystallization until essentially complete crystallization of PLA was achieved at a cooling rate of 5 °C or less. If the cooling rate was such that PLA incompletely crystallized during cooling, crystallization was completed during subsequent heating, as indicated by a cold-crystallization exotherm. Crystallization of the PLA during cooling facilitated crystallization of PEG. Increasing PEG crystallinity paralleled increasing PLA crystallinity as the cooling rate became slower. However if PEG incompletely crystallized during cooling, it did not crystallize further during subsequent heating.

Crystallinities of PLA and PEG were determined from the crystallization enthalpy in cooling thermograms and from the difference between the enthalpies of cold-crystallization and melting in subsequent heating thermograms. The values given in Table 1 are normalized to the amount of the constituent in the blend. Crystallinity determined from cooling thermograms was slightly lower than that obtained from heating thermograms. The parallel effect of cooling rate on crystallinity of PLA and PEG determined from the crystallization exotherm is shown in Fig. 3a. If the cooling rate was less than 5 °C min^{-1}, the crystallinity of PLA and PEG reached a plateau at 40 and 60%, respectively. The one-to-one correspondence between PLA crystallinity and PEG crystallinity is demonstrated by the linear relationship in Fig. 3b. The 40% crystallinity of PLA in the slow-cooled 70/30 blend approached that achieved by annealing PLA at 100 °C, which indicated that PLA essentially completely crystallized in the blend. However, crystallinity of PEG in the blend of 60% was much lower that the 94% crystallinity achieved by cooling PEG alone at 1 °C min^{-1}.

The crystalline morphology of the 70/30 blend was probed with AFM phase images. The quenched blend was too soft to microtome at ambient temperature and too sensitive to water condensation to microtome at cryogenic temperatures. The image in Fig. 4a shows a free melt surface of the quenched blend. The surface is featureless, which is consistent with an amorphous blend. The image in Fig. 4b was obtained from a microtomed surface of the blend that was cooled at 30 °C min^{-1}. It shows part of a large spherulite in a homogeneous rubbery matrix. The higher modulus crystalline material appears brighter in the phase image and the softer amorphous matrix appears darker. Higher resolution images showed that the spherulite consisted of crystalline granules rather than organized crystalline lamellae. It was not possible to differentiate PLA and PEG crystals. Cooling at 5 °C min^{-1} resulted in very large impinging spherulites, Fig. 4c. The regular banding pattern is typical of slowly cooled PLA/PEG blends [3,7,10]. The large spherulites of the slowly cooled PLA/PEG 70/30 blend were easily viewed in the polarized light microscope. Heating to 80 °C in the hotstage of the microscope in order to melt the PEG crystals did not result in visible changes to the spherulitic morphology. A similar

Table 1
Effect of cooling rate on crystallization behavior of PLA and PEG in the PLA/PEG 70/30 blend

Cooling rate (°C min^{-1})	Cooling						Subsequent heating								
	PLA crystallization			PEG crystallization			PEG melting			PLA cold-crystallization			PLA melting		
	T_C (°C)	ΔH (J g^{-1})	X_C (%)	T_C (°C)	ΔH (J g^{-1})	X_C (%)	T_m (°C)	ΔH (J g^{-1})	X_C (%)	T_C (°C)	ΔH (J g^{-1})	X_C (%)	T_m (°C)	ΔH (J g^{-1})	X_C (%)
100	–	0	0	–	0	0	–	0	0	88	−26	38	151	29	43
30	66	−3	4	8	−5	8	56	9	15	89	−14	21	150	29	43
20	70	−12	18	15	−16	27	58	20	34	89	−9	13	151	30	44
10	79	−22	32	26	−27	46	58	35	59	89	−1	1	150	30	44
5	90	−26	38	29	−33	56	59	35	59	–	0	0	151	29	43
2	98	−26	38	32	−35	59	59	36	61	–	0	0	151	30	44
1	105	−27	40	36	−36	60	59	37	63	–	0	0	151	30	44
PEG (1 °C min^{-1})	–	–	–	42	−185	94	63	191	97	–	–	–	–	–	–

observation was reported previously [7,10] and suggested that PEG crystals were located within the PLA spherulites.

It appeared that PLA slowly crystallized during cooling as large isolated spherulites that only impinged and became space-filling as crystallization approached completion. The extent to which the PLA crystallized depended on the cooling rate. Some fraction of the PEG subsequently crystallized at a lower temperature. There was a one-to-one correlation between PLA crystallinity and PEG crystallinity. However, even when PLA reached maximum crystallinity as space-filling spherulites, a significant fraction of PEG did not crystallize. This PEG fraction probably existed as a miscible blend with the amorphous PLA fraction.

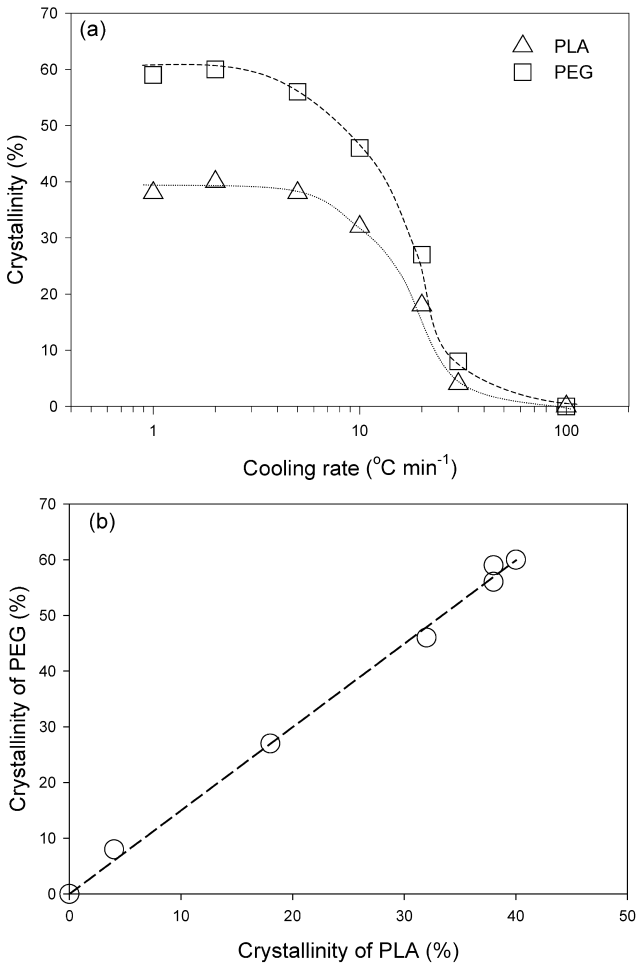

Fig. 3. Crystallinity of PLA and PEG in PLA/PEG 70/30: (a) effect of cooling rate on crystallinity of PLA and PEG; and (b) correlation between crystallinity of PLA and PEG.

3.2. Aging of crystallized PLA/PEG 70/30

The PLA essentially completely crystallized in the blend during slow-cooling, however the 60% PEG crystallinity in the slow-cooled blend was significantly lower than the achievable level of 94%. Further crystallization of PEG over time at ambient temperature might have been expected. However, a highly crystalline blend obtained by cooling at 1 °C min^{-1} exhibited no change in crystallinity over time at ambient temperature. The PEG crystallinity from melting enthalpy was 63% regardless of whether the heating thermogram was obtained immediately after cooling or after the blend had aged for 1 week at ambient temperature. Assuming that non-crystallized PEG and PLA fractions constituted a homogeneous amorphous phase in the slowly cooled blend, the weight fraction of each constituent, $W_{a,i}$, in the amorphous phase can be calculated as

$$W_{a,i} = \frac{W_i(1-\phi_i)}{W_1(1-\phi_1)+W_2(1-\phi_2)} \quad (1)$$

where W_i is the weight fraction of the constituent in the blend and ϕ_i is the crystallinity of the constituent after slow-cooling. The composition of the amorphous phase of the blend was estimated to be PLA/PEG 78/22. An amorphous blend of this composition would have T_g of about 19 °C [6]. With T_g close to ambient temperature, the kinetics of crystallization would have been too slow for PEG to crystallize much more on the time scale of aging. However, increasing the temperature should facilitate further

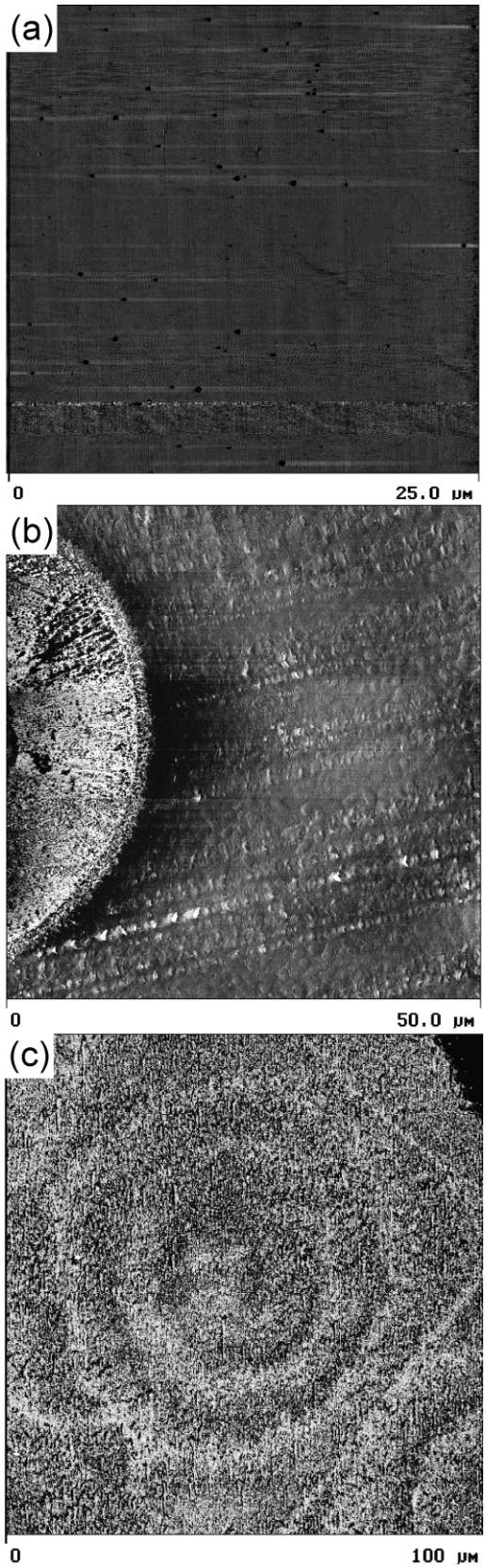

Fig. 4. AFM phase images showing the effect of cooling rate on morphology of PLA/PEG 70/30: (a) quenched; (b) cooled at 30 °C min^{-1}; and (c) cooled at 5 °C min^{-1}.

crystallization of PEG. Indeed this was observed. The PEG crystallinity increased from 63 to 76% after the slowly cooled blend was aged for 48 h at 35 °C. Aging at higher temperatures started to melt the PEG crystals.

Faster cooling rates produced blends in which PLA was not completely crystallized. Over time, an increase in stiffness of partially crystallized blends was noted. Aging of the partially crystallized blend was studied with the 70/30 composition cooled at 30 °C min^{-1}. Before aging, the amorphous phase was very soft and consequently difficult to microtome at ambient temperature. The roughness in Fig. 5a and b that is most apparent in the height image was caused by knife chatter. The AFM height and phase images obtained shortly after the blend was cooled from the melt show part of an isolated spherulite in a homogeneous amorphous matrix Fig. 5a and b. In the phase image, the spherulite is surrounded by a thin crystalline region of intermediate brightness that extends about 1–2 μm into the dark matrix. This is shown schematically in Fig. 5c.

Stiffening of the amorphous phase during aging made it possible to prepare better quality microtomed surfaces, Fig. 5d and e. Height and phase images of an isolated spherulite and the surrounding matrix after aging for 2 h at ambient conditions of temperature and humidity are shown in Fig. 5d and e. The texture of the main spherulite did not change, however the ring surrounding the spherulite increased in thickness to 5–6 μm. The crystalline ring was most apparent in phase images, Fig. 5b and e. Contrast between the main spherulite and the outer ring was provided by a modulus difference, not by a height difference on the microtomed surface. The spherulite and surrounding crystalline ring are identified as regions I and II in the schematic in Fig. 5f. Morphological features of the amorphous matrix were more evident in height images where modulus differences were not large enough to provide good phase contrast, but height differences, probably resulting from differential expansion when the film was microtomed, were revealing. After aging for 2 h, an irregular featureless region with thickness 10–20 μm was discernable around the spherulite. It is identified as region III in the schematic, Fig. 5f. Further from the spherulite the amorphous phase contained a dispersion of small domains about 200–500 nm in size. The texture in this region resembled the phase-separated morphology reported for quenched PLA/PEG blends after they aged at ambient conditions [6]. The phase-separated region is identified as region IV in the schematic, Fig. 5f.

Thermograms of the 70/30 blend cooled at 30 °C min^{-1} and aged at ambient temperature are shown in Fig. 6. Aging for 2 h resulted in an increase in PEG crystallinity from 15 to 20%, but had almost no effect on PLA crystallinity, Table 2. Further aging for 200 h resulted in only a slight increase in PEG crystallinity to 21%. Considering that the crystallinity of space-filling spherulites in blends cooled at 1 °C min^{-1} did not change with time at ambient temperature, any increase in PEG crystallinity during aging of

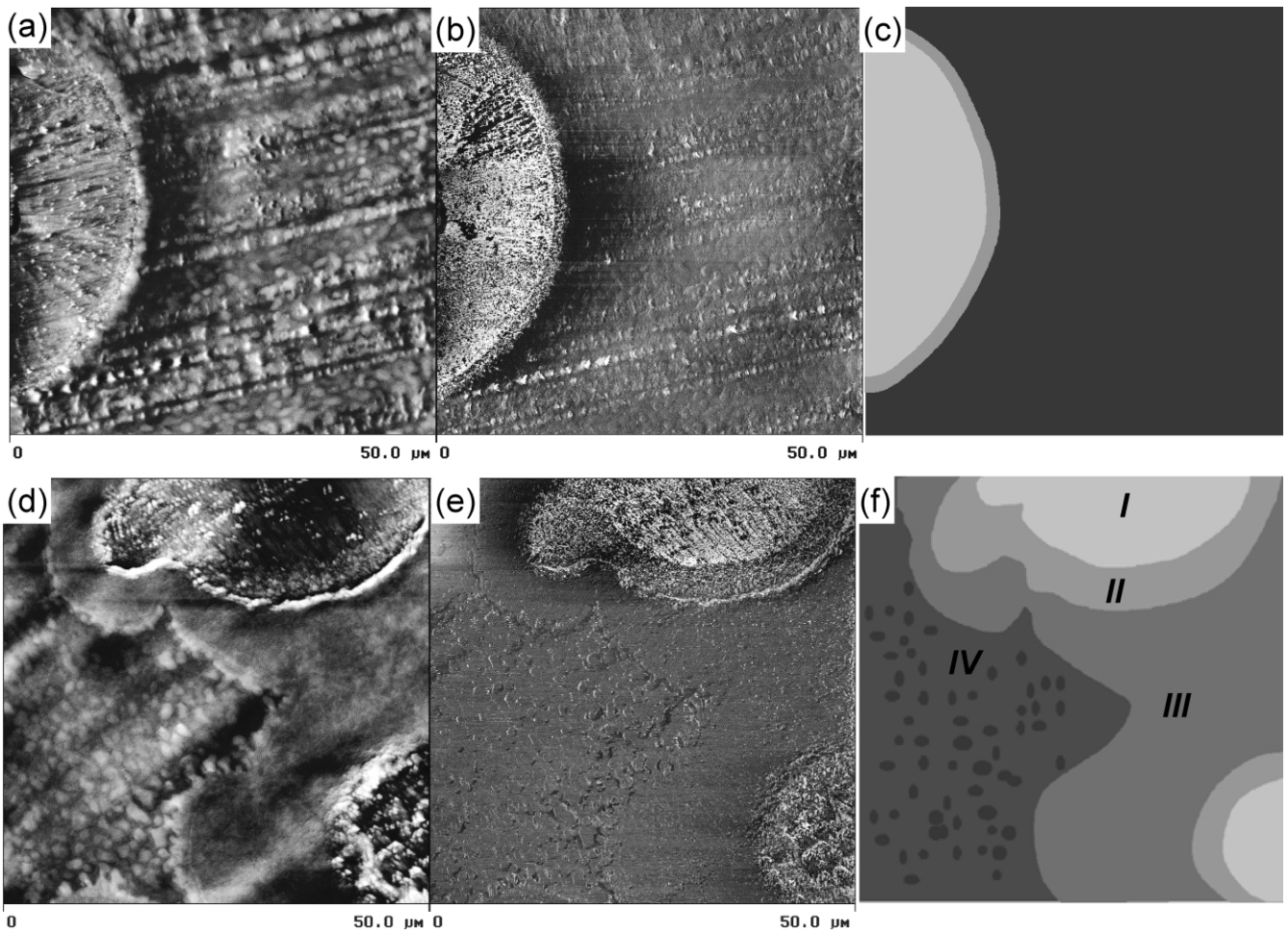

Fig. 5. AFM images showing the effect of ambient temperature aging on morphology of PLA/PEG 70/30 cooled at 30 °C min^{-1}: (a) unaged, height image; (b) unaged, phase image; (c) unaged, schematic; (d) aged 2 h, height image; (e) aged 2 h, phase image; and (f) aged 2 h, schematic.

partially crystallized blends would have occurred in the interspherulitic amorphous regions, not in the intraspherulitic amorphous regions. The increase in PEG crystallinity during aging coincided with the appearance of the crystalline outer ring on the spherulites.

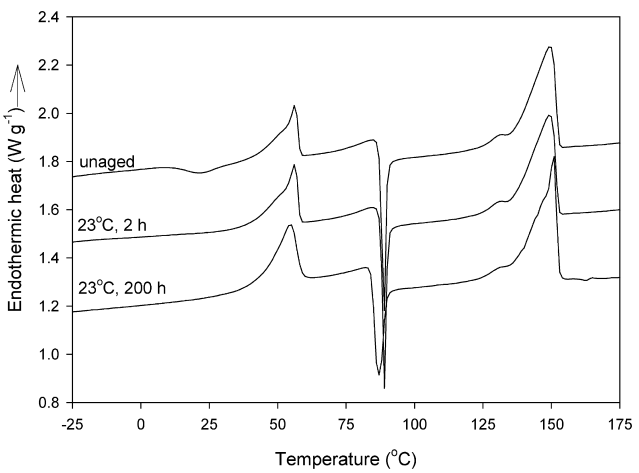

Fig. 6. Thermograms of PLA/PEG 70/30 cooled at 30 °C min^{-1} after aging at ambient temperature (23 °C) for the time indicated.

Crystallization of PEG from amorphous blends with PLA is very slow [5,6]. This is consistent with the correspondence between PLA crystallinity and PEG crystallinity in slowly cooled blends (Fig. 3a). Thus, PEG that is trapped within the spherulite crystallizes readily, whereas PEG in the amorphous matrix does not crystallize in the time frame of cooling. It is proposed that over time further epitaxial crystallization of PEG on the edges of the spherulite creates the crystalline ring on the outside of the spherulite (region II in Fig. 5f). This is consistent with an increase in PEG crystallinity over time but no change in PLA crystallinity. Diffusion of PEG to the crystallization site depletes the surrounding amorphous region of PEG and increases the T_g locally. When T_g reaches the aging temperature, diffusion slows considerably. The homogeneous region surrounding the spherulite (region III) is identified as the vitrified region of higher T_g that is depleted of PEG.

Regions of the amorphous phase that are more distant from the spherulite (region IV) are not affected by diffusion and crystallization of PEG. Although the amorphous phase does not have time to phase-separate during cooling from

Table 2
Effect of ambient temperature aging on crystallinity of PEG and PLA in PLA/PEG 70/30 cooled at 30 °C min^{-1}

Aging time (h)	PEG melting			PLA cold crystallization			PLA melting		
	T_m (°C)	ΔH (J g^{-1})	X_C (%)	T_C (°C)	ΔH (J g^{-1})	X_C (%)	T_m (°C)	ΔH (J g^{-1})	X_C (%)
0	56	9	15	89	−14	21	150	29	43
2	56	12	20	89	−14	21	149	29	43
200	55	13	21	87	−15	22	150	29	43

the homogeneous melt, it is not stable at ambient temperature and proceeds to phase-separate with formation of a stiffer PLA-rich matrix and softer PEG-rich domains. A previous study indicated that phase separation in this blend composition occurs on the time scale of hours [6].

3.3. Effect of blend composition

Thermograms of PLA/PEG blends of different compositions cooled at 1 °C min^{-1} are shown in Fig. 7a. Decreasing PEG content affected crystallization of both constituents. The crystallization temperature of PLA decreased without affecting the extent of PLA crystallization as determined from crystallization enthalpy, Table 3. The crystallization temperature of PEG decreased slightly, however the amount of PEG crystallinity decreased more than in proportion to the amount of PEG to the extent that no crystallization of PEG was detected in the 90/10 blend. Subsequent heating thermograms are shown in Fig. 7b. Melting temperatures of PEG and PLA changed only slightly with blend composition, and the melting enthalpies closely matched the corresponding crystallization enthalpies.

Thin sections taken from blends cooled at 1 °C min^{-1} and viewed in the light microscope showed space-filling spherulites in all the compositions. Blending PEG with PLA increased crystallization rate and decreased nucleation density of PLA [3]. This effect resulted in progressively larger space-filling spherulites as the PEG content of the blend increased. The texture remained unaltered when the blends were heated above the melting temperature of PEG to 80 °C, which confirmed that PEG crystals were embedded in the PLA spherulites.

The effect of cooling rate on crystallinity of PEG is shown in Fig. 8. Whereas the 70/30 blend required a cooling rate of 5 °C min^{-1} or slower to reach the maximum PEG crystallinity, the 80/20 blend required a lower cooling rate of 1 °C min^{-1} to reach the maximum crystallinity. The PLA crystallinity of 40% in all the slow-cooled blends approached that achieved by annealing PLA at 100 °C, which indicated that PLA essentially completely crystallized in all the blends. However, PEG crystallinity based on total PEG content decreased from 94% achieved by cooling PEG alone at 1 °C min^{-1} to 60% in the 70/30 blend to 44% in the 80/20 blend to essentially 0% PEG crystallinity in the 90/10 blend.

Crystallization of PLA enriched the intraspherulitic regions in PEG. After PLA crystallized, the intraspherulitic amorphous phase compositions of 70/30, 80/20 and 90/10 blends were PLA/PEG 58/42, 70/30 and 84/16, respectively, from Eq. (1), Table 3. Upon further cooling,

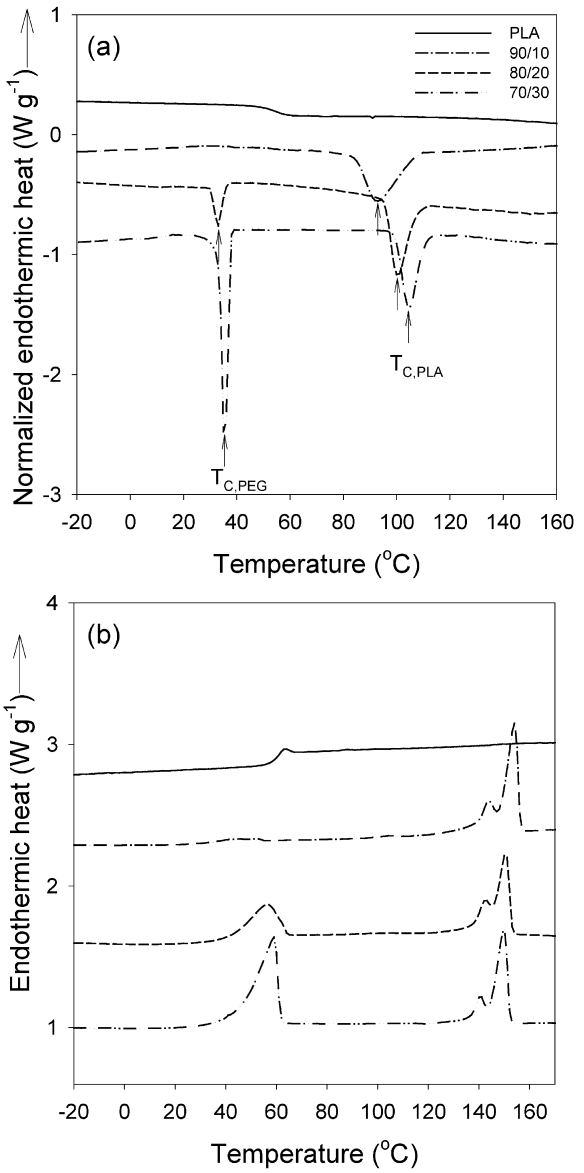

Fig. 7. Effect of PEG content on crystallization and melting of PLA/PEG blends: (a) cooling thermograms obtained with a cooling rate of 1 °C min^{-1}; and (b) subsequent heating thermograms obtained with a heating rate of 10 °C min^{-1}.

Table 3
Dependence of PEG and PLA crystallinity and amorphous composition on PEG content in PLA/PEG blends cooled at 1 °C min^{-1}

PEG content (wt%)	$T_{C,PLA}$ (°C)	$X_{C,PLA}$[a] (%)	Composition of amorphous phase before PEG crystallized (PLA/PEG)	$T_{C,PEG}$ (°C)	$X_{C,PEG}$[a] (%)	Composition of amorphous phase after PEG crystallized (PLA/PEG)
100	–	–	–	42	94	–
30	105	40	58/42	36	60	78/22
20	100	41	70/30	33	44	81/19
10	93	41	84/16	N/A	0	84/16
0	N/A	0	–	–	–	–

[a] From cooling thermogram.

PEG crystallized from the enriched melt. Two possibilities can be considered for intraspherulitic crystallization of PEG. One is that the PEG crystallized from the homogeneous melt, which depleted the amorphous phase of PEG and increased the T_g. Crystallization essentially ceased as T_g approached the crystallization temperature of PEG. Following this approach, the composition of the intraspherulitic amorphous phase, estimated from the PLA and PEG crystallinity of blends cooled at 1 °C min^{-1}, was about PLA/PEG 80/20 regardless of the initial blend composition, Table 3. The T_g of this composition from DSC was 22 °C [6].

The second possibility is that the intraspherulitic amorphous melt phase-separated into a PEG-rich phase and a PLA-rich phase as the blend cooled below the crystallization temperature of PLA. The PEG subsequently crystallized from the PEG-rich phase. Indeed, the intraspherulitic melt was in the composition range where phase separation became thermodynamically favorable as the blend cooled to the crystallization temperature of PEG [6]. However, kinetic factors are also important in the competition between PEG crystallization from a homogeneous intraspherulitic melt and phase separation with crystallization from an intraspherulitic PEG-rich phase. In the bulk, phase separation of PLA/PEG blends is slow [6]. Furthermore, AFM images of slowly cooled blends with

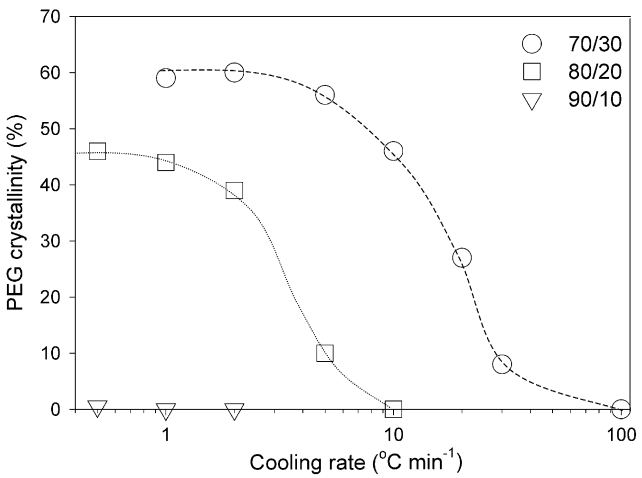

Fig. 8. Effect of cooling rate on PEG crystallinity in PLA/PEG blends of different PEG content.

space-filling spherulites did not show intraspherulitic or interspherulitic domains on the micron size scale that might have indicated phase separation [11]. In either case, considering the proximity of ambient temperature to the amorphous phase T_g and also to the crystallization and melting temperatures of PEG, it is not surprising that it is difficult to achieve stable solid state structures and properties in PLA/PEG blends.

4. Conclusions

Crystallization and aging of slowly cooled PLA/PEG blends was studied. Although the blend constituents were crystallizable, the blends could be quenched from the melt to the homogeneous amorphous glass. Alternatively, the blends could be crystallized by slowly cooling from the melt. The extent of crystallization depended on the cooling rate. The maximum crystallinity of the PLA/PEG 70/30 (wt/wt) blend was achieved with a cooling rate of 5 °C min^{-1} or less. Both PLA and PEG crystallized during slow-cooling. Proportionality between PEG crystallinity and PLA crystallinity indicated that PEG that was trapped in the intraspherulitic regions crystallized much more rapidly than PEG in the interspherulitic amorphous regions. Crystallization of intraspherulitic PEG ceased as T_g of the intraspherulitic amorphous regions approached ambient temperature. However, further crystallization of intraspherulitic PEG was possible by increasing the temperature.

In contrast to previous studies that focused on aging of amorphous quenched blends, this study examined aging of crystalline blends. The morphology of partially crystallized blends consisted of large spherulites dispersed in a homogeneous amorphous matrix. The solid state structure was not stable at ambient temperature if the amorphous phase was in the rubbery state, that is, above its T_g. Epitaxial crystallization of PEG on the edges of existing spherulites depleted the surrounding region of that constituent thereby increasing the T_g locally until vitrification essentially halted further crystallization of PEG. Regions of the amorphous phase that were more distant from the spherulites experienced a different aging process. These regions underwent phase separation without crystallization. Formation of a PLA-rich matrix with dispersed PEG-rich domains was

completely analogous to the aging process previously observed in completely amorphous quenched blends. Both aging processes altered the blend properties and increased stiffness. There was no indication that PLA crystallized further during aging.

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