

Crystallization Behavior and Mechanical Properties of Poly(ethylene oxide)/Poly(L-lactide)/Poly(vinyl acetate) Blends

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ABSTRACT: Poly(vinyl acetate) (PVAc) was added to the crystalline blends of poly(ethylene oxide) (PEO) and poly(L-lactide) (PLLA) (40/60) of higher molecular weights, whereas diblock and triblock poly(ethylene glycol)–poly(L-lactide) copolymers were added to the same blend of moderate molecular weights. The crystallization rate of PLLA of the blend containing PVAc was reduced, as evidenced by X-ray diffraction measurement. A ringed spherulite morphology of PLLA was observed in the PEO/PLLA/PVAc blend, attributed to the presence of twisted lamellae, and the morphology was affected by the amount of PVAc. A steady increase in the elongation at break in the solution blend with an increase in the PVAc content was observed. The melting behavior of PLLA and PEO in the PEO/PLLA/block copolymer blends was not greatly affected by the block copolymer, and the average size of the dispersed PEO domain was not significantly changed by the block copolymer. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 3618–3626, 2001

Key words: PEO/PLLA blend; PVAc; PEG–PLLA block copolymer; compatibilizer

INTRODUCTION

Poly(L-lactide) (PLLA) has been one of the most widely studied biodegradable polymers because of its excellent optical and mechanical properties.^{1–6} However, PLLA is expensive compared with the cost of the majority of commodity polymers. Moreover, the processibility of PLLA is rather poor and it is not easy to control the biodegradation rate of PLLA. Therefore, PLLA has been used for limited medical applications such as sutures⁷ and bone-fixation materials.⁸ Blending of biodegradable aliphatic polyesters such as PLLA with commodity polymers could be very useful in terms of improving processibility, lowering the cost, and control-

ling the biodegradation rate.^{9–13} In this study PLLA was blended with poly(ethylene oxide) (PEO), a hydrophilic commodity thermoplastic, to impart flexibility and to lower the material cost, while maintaining biodegradability. Because PLLA and PEO, especially of high molecular weights, are known to be essentially incompatible,^{10,11} poly(vinyl acetate) (PVAc) and block copolymers of poly(ethylene glycol) (PEG) and PLLA, respectively, were used as compatibilizers.

Block copolymers have been known to be one of the effective compatibilizers^{14,15} for incompatible polymer blends. They tend to reduce the size of the dispersed phase of the blend by lowering the interfacial free energy, inhibiting the macroscopic phase separation, and thus increasing the interfacial adhesion strength.¹⁵ Although many studies on the block copolymer of PEG and lactide have been reported in the literature,^{16–20} most of

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Table I Characteristics of Polymers

Polymer	Molecular Weight (M_n)	Polydispersity (M_w/M_n)	T_m ($^{\circ}\text{C}$)
PEO 20K	20,000	1.15	60
PEO 200K	200,000 ^a	—	65
PLLA (star)	55,700	3.99	148
PLLA I (linear)	37,700	2.04	178
PLLA II (linear)	160,000	—	176

^a Viscosity-average molecular weight.

them focused on the synthesis, characterization, and the hydrolytic degradation of the block copolymers. In our investigation PEG–PLLA diblock and triblock copolymers with various block lengths were employed as the compatibilizer for the immiscible PEO/PLLA blend. PVAc, on the other hand, has been known to be miscible with both PEO and PLLA. For example, Wu et al.²¹ reported that PEO/PVAc blends were miscible in the amorphous state, and McCarthy and coworkers¹² found the PLLA/PVAc blends were miscible. However, no investigation of the ternary blends of PEO/PLLA/PVAc has been published. In this study the effect of PVAc on the properties of the immiscible PLLA/PEO blend is reported. The effect of the quenching of the PEO/PLLA/PVAc ternary blend was also investigated by comparing the properties of the solution-cast–blend films with those of the melt-blend films.

EXPERIMENTAL

Materials

PEOs of two different molecular weights and PLLAs of three different molecular weights were used (Table I). PEOs were purchased from Polysciences ($M_n = 20,000$; Warrington, PA) and Aldrich ($M_v = 200,000$; Milwaukee, WI), respectively. Star-shaped PLLA¹³ ($M_n = 55,700$) was kindly provided by the Korea Institute of Science and Technology (Seoul). Linear PLLA ($M_n = 37,700$; PLLA I) was synthesized by bulk polymerizing L-lactide in the presence of stannous octoate. Higher molecular weight linear PLLA ($M_n = 160,000$; PLLA II) was purchased from Shimadzu (Tokyo, Japan).

PVAc ($M_w = 167,000$) was obtained from Aldrich. Triblock copolymer of PLLA–PEG–PLLA

was prepared by using PEGs of different molecular weights, whereas diblock copolymer of PEG–PLLA was synthesized by reacting poly(ethylene glycol) methyl ether (PEGME; molecular weight 5000) at 140 $^{\circ}\text{C}$ for 24 h. Purified reaction products were identified by FTIR and $^1\text{H-NMR}$, and the molecular weight was measured by GPC in THF. Molecular weights of PLLA blocks at both ends of the triblock copolymer were assumed to be equal because the functionality of the two end groups of PEG would be the same. A detailed experimental procedure of the block copolymer preparation was reported elsewhere.²⁰

Blend Preparation and Characterization

PEO and PLLA were mixed at a fixed weight ratio of 40 : 60 and either PVAc or the PEG–PLLA block copolymer was added in varying amounts to the PEO/PLLA mixture. Solution blending was performed in chloroform at 3 wt % with stirring for 4 h, and the blend film was obtained by evaporating the solvent at room temperature, followed by a further drying at 40 $^{\circ}\text{C}$ in vacuum for 1 week. In the case of the high molecular weight PEO/PLLA blends containing PVAc, melt blending was also carried out in a Brabender (Plasti-Corder) mixer at 200 $^{\circ}\text{C}$ for 15 min and the blend was cooled in air. The blend was then preheated at 180 $^{\circ}\text{C}$ for 2 min and compacted for 1 min under 5-ton pressure in a hot press to produce thin films, which were then immediately quenched to room temperature. The crystalline structure of the blend was investigated by X-ray diffractometry (PY-616; Phillips, The Netherlands) at a scanning rate of 0.04 $^{\circ}/\text{s}$. To investigate the morphology the sample was fractured under liquid nitrogen and the fractured surface was examined by SEM (X-650; Hitachi, Tokyo, Japan). The average diameter of the dispersed phase was determined by examining about 30 different domains of the SEM image. The tensile properties of the blend specimen (50 mm \times 5 mm \times 200 μm) were measured by UTM (Series IV; Instron) at a cross-head speed of 5 mm/min. The tensile properties of the melt blends were measured after aging of the quenched films at room temperature for 1 week and for 1 month, respectively, to monitor the effect of physical aging. Formation and growth of the PLLA spherulites in the blend were observed at 120 $^{\circ}\text{C}$ with a cross-polarized optical microscope (OPTIPHOT2-POL; Nikon, Tokyo, Japan), by melting the blend films at 200 $^{\circ}\text{C}$ for 3 min and quickly cooling to 120 $^{\circ}\text{C}$.

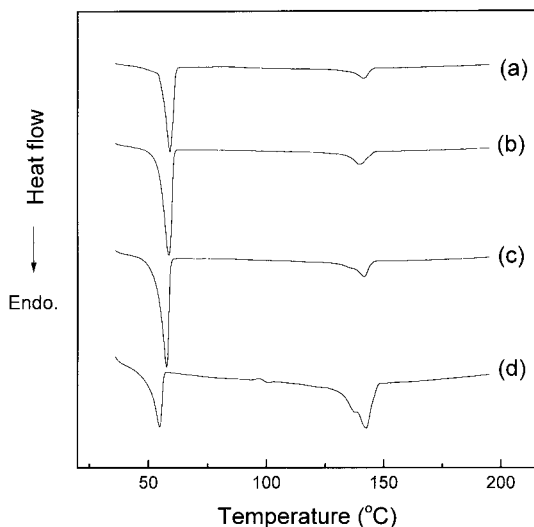


Figure 1 DSC curves of PEO 20K/star PLLA blends with 2 wt % PEG-PLLA triblock copolymers: (a) without copolymer, (b) 4KTRI2K, (c) 4KTRI4K, and (d) 4KTRI12K.

RESULTS AND DISCUSSION

PEO/PLLA/PEG-PLLA Block Copolymer System

The miscibility of a polymer blend can be evaluated by comparing the T_g of the blend with that of the constituent polymers. Unfortunately, in the PEO/PLLA blends the T_g of PLLA, which was observed around 60°C, was very close to the T_m of PEO. The accurate determination of the T_g of PLLA by a thermal method such as DSC was very difficult, because the T_g of PLLA could easily be obscured by the T_m of PEO. Therefore, we focused on the change in the melting point of the blend, as the block copolymer was introduced to the blend. In Figure 1 the DSC curve of the PEO/star PLLA 40/60 blend is compared with those of the blends containing 2 wt % of various PEG-PLLA triblock copolymers. DSC samples were heated to 200°C at a rate of 10°C/min, slowly cooled to room temperature, and reheated to 180°C at a rate of 10°C/min to record the melting temperature. To denote the structural sequences of the block copolymers a system of abbreviations was adopted. For example, 4KTRI16K is a triblock copolymer in which the PEG midblock of molecular weight of 4000 is connected to two PLLA blocks at both ends, with each PLLA block having a molecular weight of 8000. Likewise, 5KDI10K is a diblock copolymer of PEGME block of molecular weight of 5000 and PLLA block of molecular weight of 10,000. The

PEO/star PLLA blend [Fig. 1(a)] showed two endotherms, each of which corresponds to the T_m of PEO and of star PLLA, respectively, which is a clear indication that PEO and star PLLA are not miscible. All blends containing the triblock copolymer also showed two distinct endotherms, each of PLLA and of PEO, respectively [Fig. 1(b)–(d)].

The melting temperature of PLLA in the blend was nearly constant at around 141°C, whereas the T_m of PEO in the PEO/star PLLA blend shifted to lower temperatures, as the PLLA block length of the PEG-PLLA triblock copolymer increased at a constant block copolymer concentration of 2 wt %. The effect of the block copolymer concentration on the T_m is depicted in Figure 2 for the PEO/star PLLA blend containing 4KTRI12K copolymer, in which the melting point depression of PEO was most significant. However, the change in the T_m of PLLA with the change in the concentration of the block copolymer was not noticeable and the same observation was made for the PEO/linear PLLA I blend.

X-ray diffraction patterns of the PEO/PLLA blends containing various amounts of block copolymer are shown in Figure 3, along with those of PEO and PLLA. Characteristic crystalline peaks of PEO were found at $2\theta = 19.3^\circ$ and 23.6° [Fig. 3(a)], and those of PLLA were found at 16.6° and 19.1° [Fig. 3(b)]. All blends showed crystalline peaks at around 16.6° , 19.3° , and 23.6° , independent of the type and amount of the block copolymer. Only the relative intensity of the crystalline

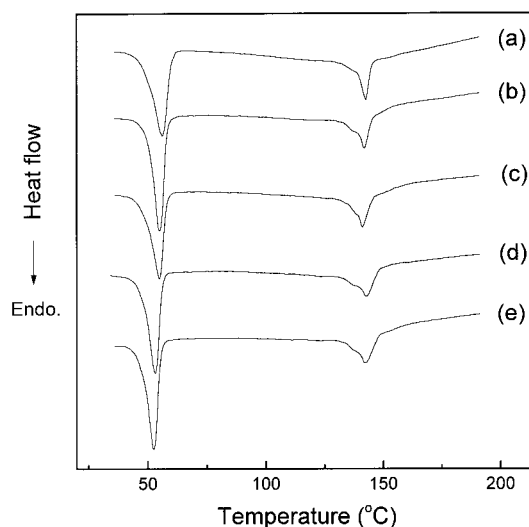


Figure 2 DSC curves of PEO 20K/star PLLA blends with 4KTRI12K: (a) 1 wt %, (b) 2 wt %, (c) 5 wt %, (d) 7 wt %, and (e) 10 wt %.

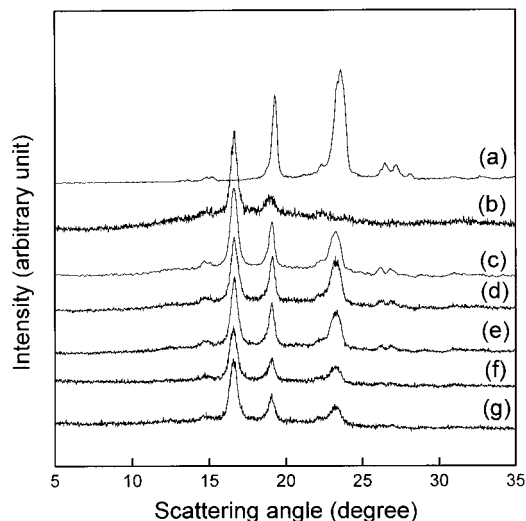


Figure 3 X-ray diffraction patterns of (a) PEO, (b) star PLLA; PEO 20K/star PLLA blend: (c) without copolymer, (d) with 2 wt % 5KDI5K, (e) with 2 wt % 5KDI20K, (f) with 2 wt % 4KTRI4K, and (g) with 2 wt % 4KTRI12K.

peaks was altered with the addition of the block copolymer, and no additional peak attributable to the cocrystallization was found. Thus, the addition of the block copolymer as the compatibilizer did not destroy or significantly change the individual crystalline structures of PEO and PLLA domains.

The size and the distribution of the dispersed phase in the blends were studied by SEM. For improved contrast of the SEM image hot metha-

nol was used to etch out the PEO domain in the surface, which is the minor component. In Figure 4 a phase-separated domain morphology is clearly observed for both the PEO/star PLLA and the PEO/linear PLLA I blends. Table II lists the average PEO domain sizes of the PEO/PLLA blends, calculated based on the SEM observation, assuming that the shape of the dispersed PEO domain was elliptical. In the absence of the copolymer the PEO/star PLLA blend showed a smaller dispersed domain than that of the PEO/linear PLLA I blend. With the addition of 2 wt % asymmetric block copolymer, the dispersed domain size became smaller as the PLLA block became longer. When the PEG block length was larger than that of the PLLA block as in 5KDI2.5K, 4KTRI2K, and 20KTRI5K, the dispersed domain size of the blend increased, probably because the block copolymer was dissolved in the dispersed phase of the blend.

It is well known that symmetric block copolymers of high molecular weights are effective in compatibilizing immiscible blends.^{19,20} Each block of the symmetric block copolymer of high molecular weight would diffuse into the corresponding constituent homopolymer of the blend, resulting in compatibilization. However, the molecular weight of each block of the block copolymer employed in our investigation was shorter than that of the constituent polymer of the blend and, as a result, the interpenetration of the block copolymer into the blend may not have occurred. DSC, X-ray diffraction, and SEM support that the

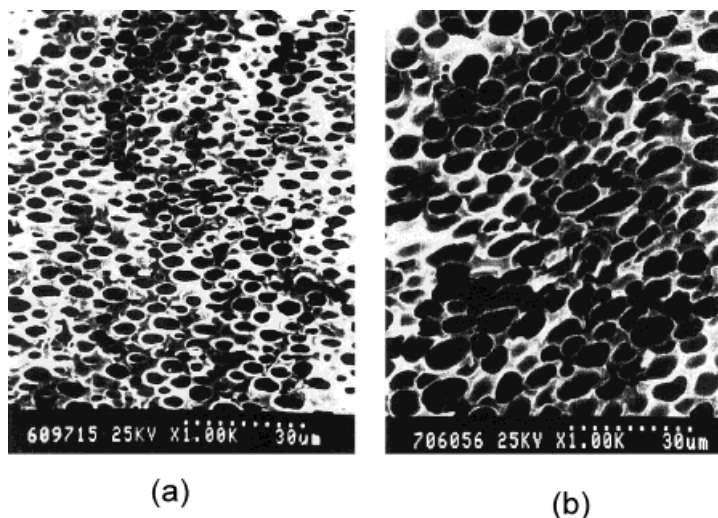


Figure 4 SEM images of PEO/PLLA blends: (a) PEO 20K/star PLLA 56K and (b) PEO 20K/linear PLLA I 38K.

Table II Effect of the PEG–PLLA Block Copolymer on the PEO Domain Sizes in PEO/PLLA Blends

	Block Copolymer ^a	Average PEO Domain Size (μm)
PEO/star–PLLA	None	3.9
	5KDI2.5K	4.9
	5KDI5K	3.6
	5KDI10K	4.0
	5KDI20K	3.9
	4KTTRI2K	4.6
	4KTTRI4K	3.5
	4KTTRI12K	3.3
PEO/linear–PLLA I	None	6.9
	5KDI5K	9.7
	10KTTRI10K	6.8
	20KTTRI5K	7.5
	5KTTRI20K	5.2

^a Concentration of the block copolymer = 2 wt %.

block copolymers used in our study were not effective in compatibilizing the crystalline PEO/PLLA blends.

PEO/PLLA/PVAc System

Because the efficacy of the PEG–PLLA block copolymers in the high molecular weight PEO/PLLA blends was expected to be only marginal, PVAc was added to the PEO 200K/linear PLLA II 160K blend and the change in the melting behavior of the blend was monitored. However, DSC results indicated that there was no significant effect of PVAc on the melting transition of the PEO/PLLA blend. X-ray diffraction patterns of the blends prepared by solution blending are shown in Figure 5 and those of the melt blends are shown in Figure 6. All the crystalline peaks characteristic of both PEO and PLLA were observed in the solution and melt blends, regardless of the presence of PVAc. However, the crystalline peak at 16.5° , attributed to PLLA of the melt blends, broadened and became weaker as the PVAc concentration was increased. PVAc may have retarded the crystallization of PLLA, whose crystallization rate was much slower than that of PEO.

Figure 7 displays the cross-polarized optical micrographs of PLLA spherulites grown from the melt blends containing different amounts of PVAc at 120°C . Because the T_m of PEO is lower than 120°C , only PLLA in the blend could crystallize at 120°C . Independent of the amount of PVAc, a ringed morphology²² of PLLA was evi-

dent in the PEO/PLLA blends that was different from the spherulitic morphology of the melt-grown pure PLLA.³ Because the ringed pattern is associated with the spatial twisting of lamellae, the appearance of such a pattern in the PEO/PLLA blend may indicate that the presence of PEO has altered the aggregation and thus caused the twisting of PLLA lamellae. This phenomenon is likely to occur in the PEO/PLLA blends when PEO is predominantly entrapped in the PLLA interlamellar regions after PLLA

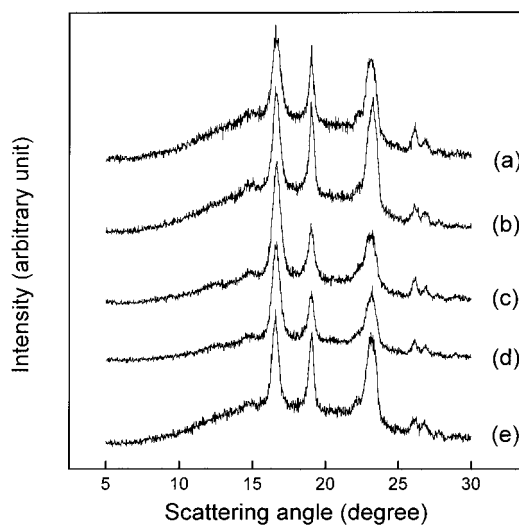


Figure 5 X-ray diffraction patterns of the PEO 200K/PLLA 160K solution blend: (a) without PVAc, (b) with 2 wt % PVAc, (c) with 5 wt % PVAc, (d) with 7 wt % PVAc, and (e) with 10 wt % PVAc.

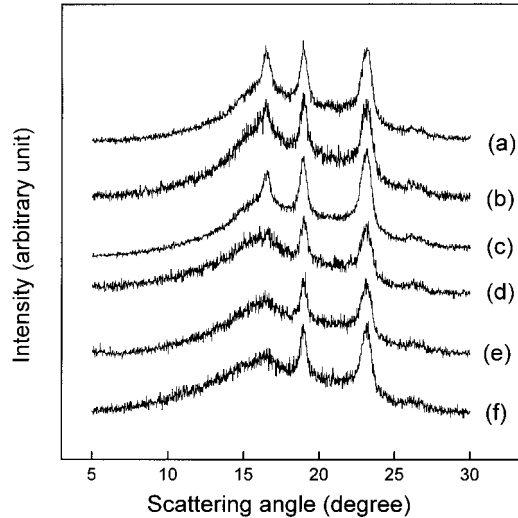


Figure 6 X-ray diffraction patterns of the PEO 200K/PLLA 160K melt blend: (a) without PVAc, (b) with 2 wt % PVAc, (c) with 5 wt % PVAc, (d) with 7 wt % PVAc, (e) with 10 wt % PVAc, and (f) with 20 wt % PVAc.

was crystallized.²² Meanwhile, as the PVAc content in the blend increased, the PLLA spherulite became increasingly irregular, and the sup-

pression of the Maltese cross extinction pattern was remarkable, especially in Figure 7(d). Thus, PVAc was believed to be entrapped in the PLLA spherulites.

The linear isothermal growth rate of PLLA spherulites at 120°C was obtained by plotting the spherulite radius against time. In the absence of PVAc the spherulitic growth rate of PLLA would increase when PEO was added. Because of a low T_g , PEO would act as a diluent that promotes molecular mobility required for the crystallization of PLLA. Upon adding PVAc to the PEO/PLLA blend, however, the spherulitic growth rate of PLLA decreased with an increase in the PVAc content (Fig. 8). The effect of PVAc on the spherulitic growth rate of PLLA in the blend can be described by the Turnbull–Fisher theory.²³ According to the theory the temperature dependency of the isothermal spherulitic growth rate (G) of a polymer may be described by

$$G = G_0 \exp[-\Delta F^\circ/kT] \exp[-\Delta\Phi^\circ/kT] \quad (1)$$

where G_0 is a constant governing the absolute crystal growth rate, ΔF° is the free energy of the

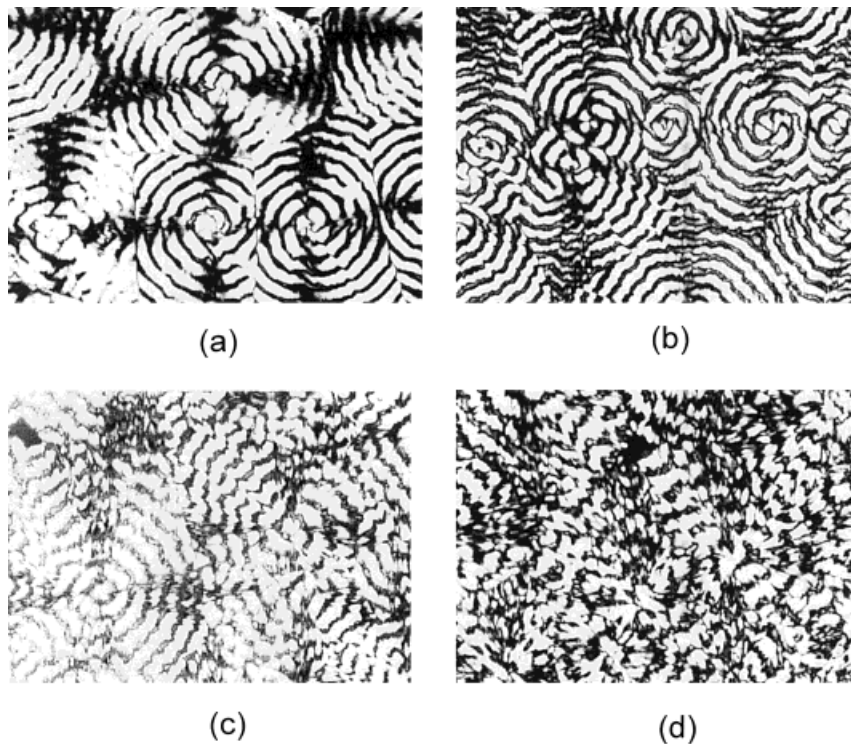


Figure 7 Optical micrographs of PLLA spherulites grown at 120°C from the PEO 200K/PLLA 160K blends: (a) without PVAc, (b) with 2 wt % PVAc, (c) with 7 wt % PVAc, and (d) with 10 wt % PVAc.

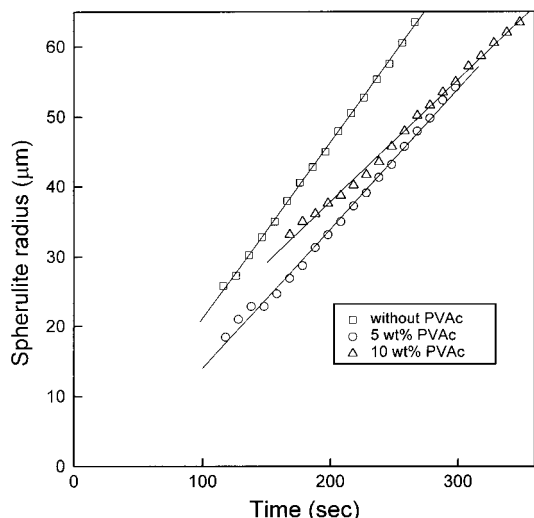


Figure 8 Change in the PLLA spherulite radius with time at 120°C in the PEO 200K/PLLA 160K blend.

transport process through the liquid–solid interface, $\Delta\Phi^\circ$ is the free energy for the formation of a nucleus of the critical size, k is the Boltzmann constant, and T is the absolute temperature. The PEO/PLLA/PVAc blend may be assumed to form a compatible blend because the optical microscope observation confirmed the presence of a one-phase melt just prior to the crystallization. Moreover, many references establish that the PEO/PVAc blend,^{21,24} the PEO/PLLA blend,^{10,22,25} and the PLLA/PVAc blend¹² are compatible in the melt. Thus, eq. (1) can be applied to the PEO/PLLA/PVAc blend, for which ΔF° may be taken from the Williams–Landel–Ferry time–temperature superposition principle²⁴:

$$\Delta F_{\text{blend}}^\circ = \frac{C_1 T_c}{C_2 + T_c - T_g} \quad (2)$$

where T_c is the crystallization temperature and C_1 and C_2 are constants. In eq. (2) F_{blend}° should always be greater than $\Delta F_{\text{polymer}}^\circ$ if the T_g of the blend is lower than that of the polymer as a result of adding the low T_g component. Meanwhile, $\Delta\Phi_{\text{blend}}^\circ$ could be related to $\Delta\Phi_{\text{polymer}}^\circ$ as follows:

$$\Delta\Phi_{\text{blend}}^\circ = \Delta\Phi_{\text{polymer}}^\circ - \frac{2\sigma K T_m T_c \ln v_2}{b_0 \Delta H \Delta T} \quad (3)$$

where σ is the surface free energy, K is a positive constant, v_2 is the volume fraction of the crystallizable component, b_0 is the monomolecular layer

of a fixed thickness, ΔH is the enthalpy change on crystallization, and ΔT is the degree of supercooling ($\Delta T = T_m^\circ - T_c$). It should be noted that the second term in the right-hand side of eq. (3), $-[(2\sigma K T_m T_c \ln v_2)/(b_0 \Delta H \Delta T)]$, is always positive and that $\Delta\Phi_{\text{blend}}^\circ > \Delta\Phi_{\text{polymer}}^\circ$. Thus, when the contribution of ΔF° to the isothermal spherulitic growth rate is assumed to be negligible, the spherulitic growth rate of the blend is lower than that of the crystallizable component of the blend. When PEO was added to PLLA, the decrease in ΔF° was larger than the increase in $\Delta\Phi^\circ$ because the T_g of PEO ($\sim -60^\circ\text{C}$) was much lower than that of PLLA ($\sim 60^\circ\text{C}$). Thus, the spherulitic growth rate of PLLA increased with the addition of PEO. When PVAc was introduced to the PEO/PLLA blend, the spherulitic growth rate of PLLA decreased compared to that of PLLA in the PEO/PLLA blend because the T_g of PVAc ($\sim 30^\circ\text{C}$) was higher than that of PEO ($\sim -60^\circ\text{C}$).

The tensile strength and elongation at break of the solution and the melt PEO/PLLA blends are compared as a function of the PVAc content in Figures 9–11. At the same PVAc loading the tensile strength of the solution blend was higher than that of the melt blend aged for 1 week at room temperature and the elongation at break was the inverse of tensile strength. In the solution blend the addition of flexible PVAc chains caused a decrease in the tensile strength and an increase in the elongation at break. Optimum properties were obtained with 2 wt % of PVAc in the solution

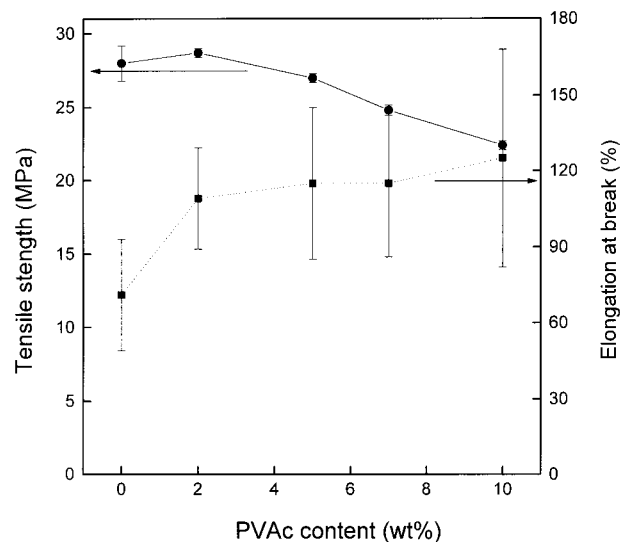


Figure 9 Change in the tensile strength and the elongation at break of PEO 200K/PLLA 160K solution blend.

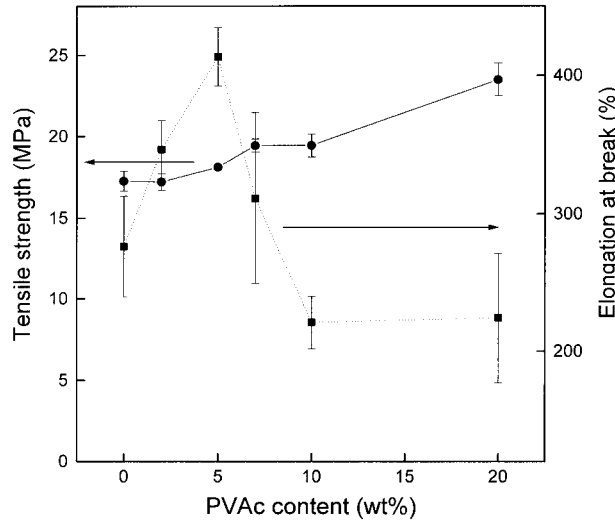


Figure 10 Change in the tensile strength and the elongation at break of PEO 200K/PLLA 160K melt blend (aged for 1 week).

blend, where the elongation at break was increased significantly without a drastic reduction in the tensile strength. Meanwhile, the tensile strength of the melt PEO/PLLA blends, which were aged for 1 week, increased with an increase in the PVAc concentration up to 5 wt % and then leveled off, a phenomenon that could be explained by the combined effect of physical aging and the presence of PVAc. For the PVAc concentration above 5 wt % the tensile strength of the melt PEO/PLLA blends no longer increased with the PVAc content because the presence of PVAc offset the physical aging effect. McCarthy and coworkers¹² also found a similar phenomenon for the PLLA/PVAc melt blends. The elongation of the melt PEO/PLLA blends that were aged for 1 week did not decrease monotonically with the PVAc content. Indeed, the elongation decreased with the PVAc content up to 2 wt %, then remained relatively constant up to 10 wt % and decreased again around 20 wt % of PVAc, which clearly indicates that the continuous decrease in the elongation with an increase in the PVAc content was slowed down by the presence of PVAc, especially up to 10 wt % of PVAc.

The same behavior was again reported by McCarthy and coworkers¹² for the PLLA/PVAc blends, in which both the effect of physical aging and the synergistic effect of PVAc on the elongation were observed. Based on the tensile properties of the PEO/PLLA/PVAc solution and melt blends, it may be concluded that the compatibilizing

effect of PVAc on the PEO/PLLA blend was most pronounced at less than 5 wt %. If the quenched PEO/PLLA/PVAc blend is further aged at room temperature, the effect of physical aging is expected to become even more apparent. As shown in Figures 10 and 11, at the same PVAc concentration the tensile strength of the blend aged for 1 month was higher, yet the elongation of the same blend was lower than that of the blend aged for 1 week, respectively.

CONCLUSIONS

PVAc and PEG-PLLA diblock and triblock copolymers were used as the compatibilizer for the crystalline PEO/PLLA (40/60) blend. The change in the melting point, the crystalline structure, the domain size of the dispersed phase, and mechanical properties of the ternary blends were investigated. X-ray diffraction studies indicated that the crystallization of PLLA in the PEO/PLLA/PVAc blends was retarded by PVAc and SEM showed that the ringed spherulitic morphology of PLLA resulting from twisted lamellae was altered significantly when the PVAc concentration increased. The compatibilizing effect of PVAc was most prominent when the PVAc concentration was less than 5 wt %. In particular, a steady increase in the elongation at break of the solution blend was pronounced with an increase in the PVAc concentration. In the PEO/PLLA/PEG-

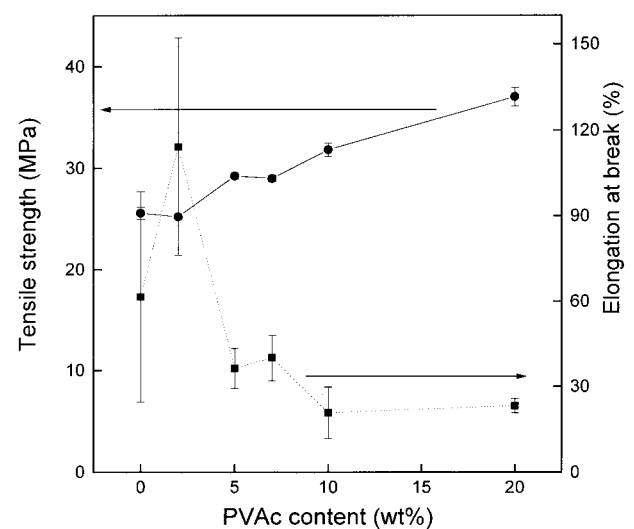


Figure 11 Change in the tensile strength and the elongation at break of PEO 200K/PLLA 160K melt blend (aged for 1 month).

PLLA block copolymer blends the melting behavior of PLLA and PEO was not greatly affected and the dispersed domain size was not significantly changed by the block copolymer, indicating little evidence of compatibilization, outcomes that may both occur because the molecular weight of each block of the block copolymer was lower than that of the constituent polymer in the blend.

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