

Miscibility in blends of liquid crystalline copolyester and semicrystalline poly(ethylene-2,6-naphthalene dicarboxylate)

Jia-Chong Ho, Tai-Ching Lin, Kung-Hwa Wei*

Department of Materials Science and Engineering, National Chiao Tung University, Hsinchu 30049, Taiwan, ROC

Received 7 December 1999; received in revised form 18 February 2000; accepted 29 February 2000

Abstract

The miscibility in blends of random liquid crystalline copoly(oxybenzoate-ethylene terephthalate) at a molar ratio of 60:40 (P64) and semicrystalline poly(ethylene-2,6-naphthalene dicarboxylate) (PEN) were investigated with differential scanning calorimetry, wide angle X-ray diffraction and polarized optical micrography. It was found that P64 and PEN were partially miscible as evidenced from the appearance of a single glass transition temperature for each blend at different compositions. Furthermore, the Flory–Huggins interaction parameter, χ_{12} , for P64 and PEN was determined to be -1.13 through the melting point depression analysis, indicating miscibility in blends of P64 and PEN at the melt state. The coherence lengths of PEN in the presence of a small amount of P64, around 3%, were larger than that in pure PEN, implying the regularity of PEN crystals in the blends with low P64 content being more perfect than that of the pure PEN. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Liquid crystalline copolyester; Miscibility; Semicrystalline copolyester

1. Introduction

Thermotropic liquid crystalline polymers (TLCPs) exhibit low melt viscosity and high modulus in the oriented direction in the solid form. Blending TLCPs with amorphous or crystalline polymers to form in-situ organic polymer composites appeared to be very attractive because of advantages in lowering the viscosity of amorphous or crystalline polymers during processing and in reinforcing the final mechanical properties of the matrix polymer [1–4]. However, liquid crystalline polymer chains are very stiff, and the enthalpy of mixing a rigid-rod polymer with a flexible-chain polymer was mostly positive; thus the entropy gained in the mixing was usually too small to compensate for the enthalpy gained. This generally led to phase-separated systems. To our knowledge, there were only several cases of miscibility in liquid crystalline polymer blends reported. They are blends of copoly(oxybenzoate-ethylene terephthalate) (POB–PET)/polycarbonate (PC) [5–7], POB–PET/poly(ether imide) (PEI) [8], POB–PET/poly(butylene terephthalate) (PBT) [9], POB–PET/poly(hexamethylene terephthalate) (PHMT) [10], POB–PET/poly(ethylene terephthalate) (PET) [11,12] and POB–PET/polyamide 6 [13]. The miscibility in the cases of POB–PET/PC, POB–PET/PBT and POB–PET/PHMT were found to

increase with the extent of transesterification between POB–PET and PC, PBT or PHMT.

Poly(ethylene-2,6-naphthalene dicarboxylate) (PEN) is a new aromatic polyester that differs from poly(ethylene terephthalate) (PET) in the double aromatic rings of the naphthalate group instead of a single one present in PET. The naphthalene moiety in PEN provides stiffness to the linear polymer backbone. The glass transition temperature (T_g), the crystallization temperature (T_c) and the melting temperature (T_m) were 120, 190 and 260°C, respectively. The oxygen permeability of PEN is approximately one-quarter to one-fifth of that of PET. PEN can be a good candidate for hot-fill and high barrier packaging applications [14–16]. There are two known crystal modifications of PEN. The first one was the α -form crystal, and the unit cell of the α -form crystal was a triclinic unit cell with the unit-cell parameters $a = 0.651$ nm, $b = 0.575$ nm, $c = 1.32$ nm, $\alpha = 81.33^\circ$, $\beta = 144^\circ$, $\gamma = 100^\circ$ as determined by Mencik [17]. The density of the α -form is 1.407 g cm⁻³, with one chain passing through each unit cell of the α -form. The naphthalene planes are nearly parallel to the ($\bar{1}10$) plane. The second one was the β -form crystal. The β -form is also a triclinic unit cell with the unit-cell parameters [18] of $a = 0.926$ nm, $b = 1.559$ nm, $c = 1.273$ nm, $\alpha = 121.6^\circ$, $\beta = 95.57^\circ$, $\gamma = 122.52^\circ$. The density of the β -form is 1.439 g cm⁻³, with four chains passing through each unit cell of the β -form. The chains

* Corresponding author. Tel.: +886-3-5731871; fax: +886-3-5724727.

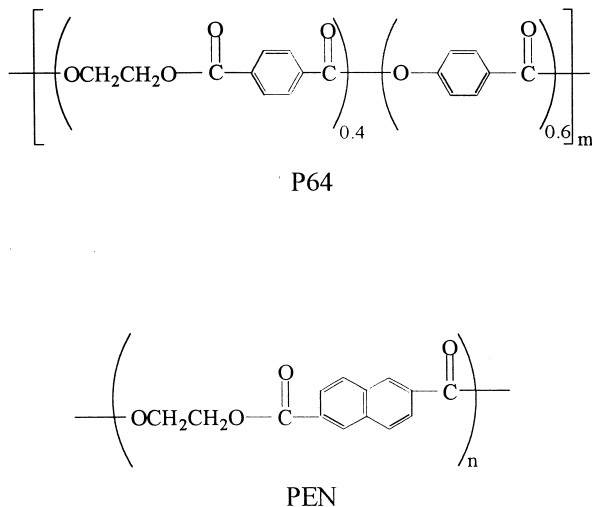


Fig. 1. The chemical structures of P64 and PEN.

are not completely extended, and every naphthalene is twisted by 180°. At crystallization temperatures up to 200°C only the α -form crystal of PEN is formed. As the crystallization temperatures increased from 240°C up to melting temperature, the β -crystal of PEN formed mainly [18]. Additionally, the amorphous form can be induced to the α -form of the PEN film with *N,N*-dimethylformamide and the β -form with dioxane [19].

Copoly(oxybenzoate-ethylene) at a molar ratio 60:40 (P64) is a random liquid crystalline copolyester having T_g , T_c , and T_m at 59.8, 103.3 and 194.6°C, respectively [20,21]. In this study, we would like to investigate the miscibility and the induced crystal size changes in the binary blend of liquid crystalline P64 and semicrystalline PEN by using differential scanning calorimetry, wide angle X-ray diffraction and polarized optical microscopy.

2. Experimental

Liquid crystalline POB–PET at a mole ratio of 60:40 was obtained from Unitika Ltd, Japan, and it was termed P64. Poly(ethylene-2,6-naphthalene dicarboxylate) was purchased from Aldrich, and it was termed PEN. The chemical structures of P64 and PEN are shown in Fig. 1. The solution blending of P64 and PEN was carried out by dissolving both polymers in 100 ml of dichloroacetic acid. The concentration of the solution containing P64 and PEN was 2% by weight. The weight ratios of P64 to PEN in the solution were 15:85, 30:70, 50:50, 70:30 and 80:20. The polymer solutions were then cast onto glass slides and were dried under vacuum at 100°C for 72 h in an oven for removing the solvent. The thermal gravimetric analysis of the dried blends showed no appreciable weight loss up to 350°C, indicating a complete removal of the solvent. The thermal

analysis of the blends was carried out with a DuPont 2910 differential scanning calorimetry (d.s.c.). The d.s.c. samples were heated from 25 to 320°C at a heating rate of 40°C/min under nitrogen. Then, the samples were quenched to 25°C. The samples were heated again from 0 to 320°C at a heating rate of 20°C/min. The d.s.c. curves of the samples were taken during the second heating. The midpoints in glass transitions of the d.s.c. curves were taken as the glass transition temperatures (T_g). The peak temperatures of the melting endothermic of the annealed blends from d.s.c. were determined as the melting temperatures. In the equilibrium melting temperature measurement, the samples were heated from 25 to 320°C at a heating rate of 40°C/min under nitrogen. Subsequently, the samples were quenched to the crystallization temperature, and were maintained at the crystallization temperature for 4 h. For the polarized optical microscopy and the wide angle X-ray diffraction analyses, the specimens were heated from room temperature to 320°C, and were maintained at 320°C for 1 min for wiping out the previous thermal history of these samples. The specimens were then quenched to 200°C (crystallization temperature) and were annealed at 200°C for 4 h. After the annealing, the samples were quenched in liquid nitrogen again. The birefringence of these samples was obtained using a Carl Zeiss Axiophot microscope equipped with a Mettler FP82HT hot stage. Wide angle X-ray diffraction of these samples were performed with a MAC Science MXT-3 X-ray diffractometer using Cu K α radiation with a voltage of 50 kV and a current of 200 mA. The diffraction patterns were recorded with a step size of 0.02° from $2\theta = 5$ to 35°.

3. Results and discussion

The d.s.c. curves of P64/PEN blends at various compositions are shown in Fig. 2, and the obtained T_g , T_c , T_m , the crystallization exothermic enthalpy (ΔH_c) and the melting endothermic enthalpy (ΔH_m) are given in Table 1. In Fig. 2, a composition-dependent T_g appeared in each of the d.s.c. curves of the P64/PEN blends. The T_g of the P64/PEN blends increased slightly with P64 content in the blends. The Fox equation [22] and the Gordon–Taylor equation [23] were used to predict the glass transition temperatures of the P64/PEN binary blends, and they are given in Eqs. (1) and (2), respectively

$$\frac{1}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}}, \quad (1)$$

$$\frac{1}{T_g} = \frac{w_1 + kw_2}{w_1 T_{g1} + kw_2 T_{g2}} \quad (2)$$

where T_{gi} and w_i ($i = 1, 2$) are the glass transition temperature and the weight fraction of polymer component i , respectively, and T_g the glass transition temperature of the blend. In the Gordon–Taylor equation, the adjustable parameter k is related to the intensity of the interaction forces

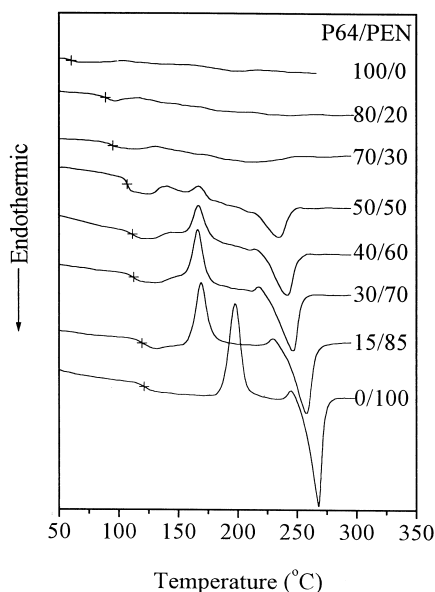


Fig. 2. The d.s.c. curves of the P64/PEN blends at various compositions.

between the constituents in the blend. The single T_g of the P64/PEN blends at various compositions agreed well with the predicted values by the Gordon–Taylor equation with $k = 0.30$ as shown in Fig. 3. This indicated a medium interaction between the amorphous phases of P64 and PEN. In Table 1, the T_c s of P64 and PEN were 103.3 and 194.9°C, respectively, and the T_c and ΔH_c decreased with the concentration of P64 in the P64/PEN blends. In the cases of the 40:60 and the 50:50 P64/PEN blends, there were two crystallization peaks in their d.s.c. curves. This indicated that the crystalline phases of the 40:60 and the 50:50 P64/PEN blend were not miscible. The miscibility in crystalline polymer blends can also be studied through the melting depression analysis. The T_m s of P64 and PEN were 194.6 and 265.3°C, respectively, and the T_m s are 257.5, 246.2, 234.0 and

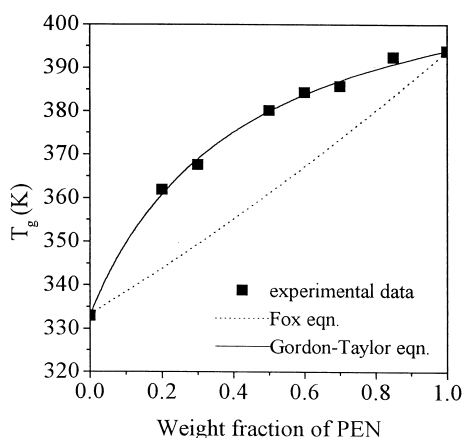


Fig. 3. The glass transition temperatures of the P64/PEN blends: (■) experimental data; (···) predicted by Fox equation; (—) predicted by Gordon–Taylor equation.

Table 1
Thermal analysis results of the P64/PEN blends

P64/PEN	T_g (°C)	T_c (°C)	ΔH_c (J/g)	T_m (°C)	ΔH_m (J/g)
0:100	120.7	194.9	44.5	265.3	46.9
15:85	119.3	169.1	34.6	257.5	44.8
30:70	112.6	166.2	25.8	246.2	32.3
40:60	111.2	144.8, 166.4 ^a	19.7	241.6	28.6
50:50	107.0	139.6, 166.1 ^a	13.5	234.0	20.8
70:30	94.4	125.6	2.8	206.3	11.4
80:20	88.7	113.5	2.1	199.5	8.6
100:0	59.8	103.3	1.6	194.6	3.1

^a 40:60 and 50:50 P64/PEN blends exhibit two crystallization peaks.

206.3°C for the 15:85, 30:70, 50:50 and 70:30 P64/PEN blends, respectively, as given in Table 1. The equilibrium melting point depression of semicrystalline polymers can be predicted by the Hoffman–Weeks equation from the equilibrium thermodynamics [24,25], as given in the following [26]:

$$T'_m = \frac{T_c}{\gamma} + \left(1 - \frac{1}{\gamma}\right)T_m^\circ \quad (3)$$

where T'_m and T_m° are the measured melting temperature and the equilibrium melting temperature, respectively, T_c the crystallization temperature, γ the proportional factor between the initial lamellar thickness, l^* , and the final lamellar thickness, l

$$\gamma = l/l^* \quad (4)$$

A number of polymer crystals thicken either isothermally at T_c or upon heating to the melting temperature, the lamellar thickness at the time of melting, l , may be greater than the initial lamellar thickness, l^* . γ is generally related to the crystallization temperature, the time and the heating conditions up to the melting temperature. At $\gamma = 1$, the polymers do not exhibit isothermal lamellar thickening. If T'_m is equal to T_c , the crystal is an inherently unstable one. γ is determined by the slope of the T'_m vs. T_c line, and T_m° is obtained as the intersection points between the $T'_m = T_c$ line and the T'_m vs. T_c line. The Hoffman–Weeks plots of PEN and the P64/PEN blends are shown in Fig. 4, and the obtained γ and T_m° are given in Table 2. In Table 2, the values of γ are found to vary from 1.34 to 1.71 for the pure PEN and the P64/PEN blends. This phenomenon can be interpreted in terms of PEN's relaxation behavior. The α -relaxation behavior of PEN is similar to that of PEEK, PPS, PET, Nylons and it-PS [27–31], where they did not display a distinctive crystalline α -relaxation in the temperature range investigated. PEN, PEEK, PPS, PET, Nylons and it-PS are therefore not expected to exhibit lamellar thickening under isothermal crystallization condition that resulted in a small γ value. The γ value for the P64/PEN blends being larger than that for pure PEN indicated that the crystal thickening during isothermal crystallization formed a more stable crystal of PEN in the P64/PEN blends, and it was similar to that

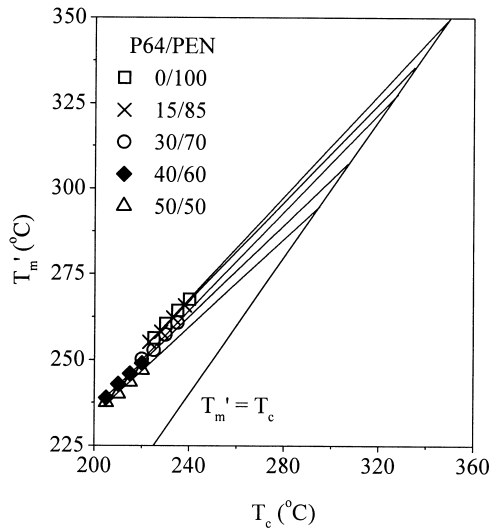


Fig. 4. The Hoffman–Weeks plots for PEN and the P64/PEN blends.

of the PBT/PETG blend [32]. The equilibrium melting point of the pure PEN is 349.5°C, and the equilibrium melting point for the 70:30 P64/PEN blend is 279.3°C as given in Table 2. The Flory–Huggins interaction parameter in a miscible semicrystalline polymer blend can be determined by the extent of the equilibrium melting point depression through an equation derived by Nishi and Wang [33]

$$\frac{1}{T_m^o} - \frac{1}{T_m^o} = \frac{-RV_2}{\Delta H_2 V_1} \left[\frac{\ln \phi_2}{m_2} + \left(\frac{1}{m_2} - \frac{1}{m_1} \right) (1 - \phi_2) \right] - \frac{RV_2}{\Delta H_2 V_1} \chi_{12} (1 - \phi_2)^2. \quad (5)$$

The subscripts 1 and 2 denoted the amorphous and the crystalline components, respectively. In Eq. (5), T_m^o and T_m^o are the equilibrium melting points of the pure polymer and the blend, respectively, V the molar volume of the polymer repeating unit, ϕ_2 the volume fraction of the component in the blend, ΔH_2 the enthalpy of fusion of the crystalline polymer, m_i ($i = 1, 2$) the degree of polymerization, R the universal gas constant, and χ_{12} the Flory–Huggins interaction parameter. When m_1 and m_2 are very large, Eq. (5) can be reduced to the following form:

$$\frac{1}{T_m^o} - \frac{1}{T_m^o} = \frac{RV_2}{\Delta H_2 V_1} \chi_{12} (1 - \phi_2)^2. \quad (6)$$

Table 2
The equilibrium melting points and the γ of the P64/PEN blends

P64/PEN	T_m^o (°C)	γ
0:100	349.5	1.34
15:85	336.2	1.38
30:70	326.8	1.39
40:60	307.2	1.50
50:50	294.5	1.56
70:30	279.3	1.71

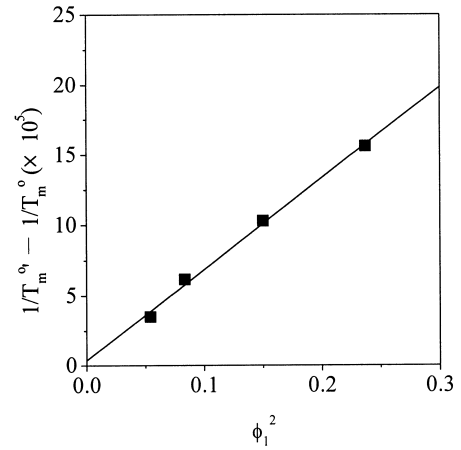


Fig. 5. The plots for determining the Flory–Huggins interaction parameter from the equilibrium melting point measurements of PEN and the P64/PEN blends.

In Eq. (6), the parameters used were $V_1 = 106.29 \text{ cm}^3/\text{mol}$ [34], $V_2 = 182.82 \text{ cm}^3/\text{mol}$ [35], and $\Delta H_2 = 25 \text{ kJ/mol}$ [36]. $T_m^o = 349.5^\circ\text{C}$ was used as the equilibrium melting point of PEN in Eq. (6) for these calculations. Eq. (6) was used to fit the equilibrium melting points of the P64/PEN blends, and the results are shown in Fig. 5. In Fig. 5, the slope of this line was $-(RV_2/\Delta H_2 V_1)\chi_{12}$, and the Flory–Huggins interaction parameter for the P64/PEN blends obtained is -1.13 . The negative value of χ_{12} indicated that P64 and PEN were miscible in the melt state.

For the X-ray diffraction study, the P64/PEN blends were treated by first quenching from the melt state and then being annealed at 200°C for 4 h. In Fig. 6, the annealed PEN exhibited three strong diffraction peaks at $2\theta = 15.6, 23.3$ and 27.0° , respectively, and these peaks are attributed to the (010), (100) and ($\bar{1}10$) planes of the α -form crystal of PEN. Moreover, the two weak peaks at $2\theta = 19.4$ and 20.3° are

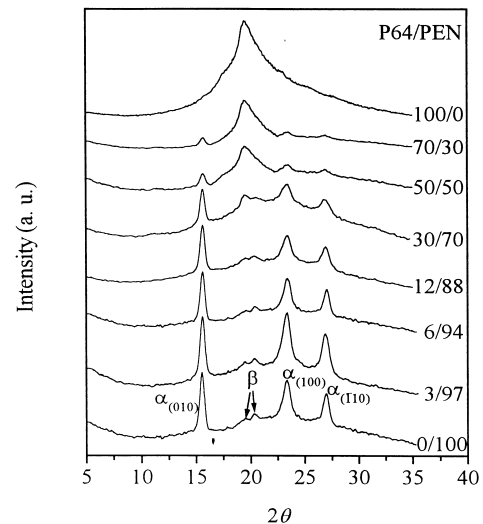


Fig. 6. The X-ray diffraction patterns of the P64/PEN blends.

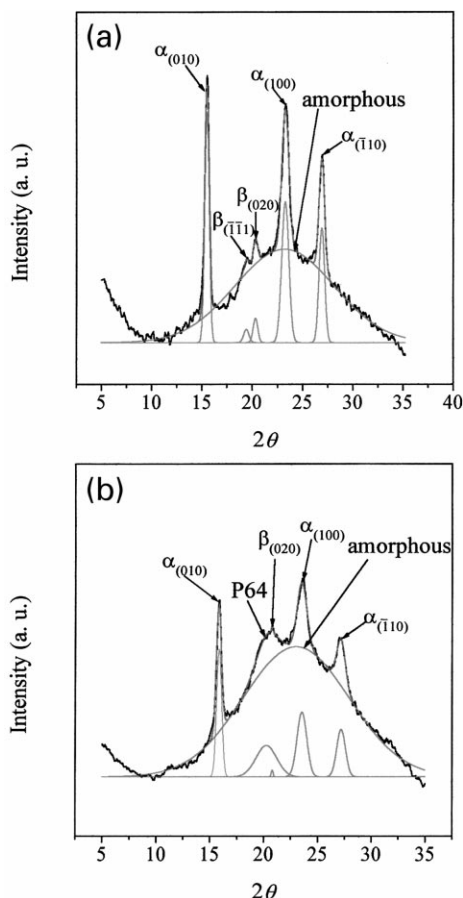


Fig. 7. The deconvolution curves of the X-ray diffraction curve: (a) pure PEN; and (b) the 30:70 P64/PEN blend.

caused by the $(\bar{1}\bar{1}1)$ and (020) planes of the β -form of PEN. P64 displayed a broad diffraction peak at $2\theta = 19.6^\circ$. The portion of the α -form of PEN in the P64/PEN blends decreased with the increasing amount of P64. The positions of the X-ray diffraction peaks of the P64/PEN blends were not shifted as compared to that of pure PEN, indicating that the pure PEN crystal structure remained in the P64/PEN blend. The crystal size of the semicrystalline polymer can be estimated by using the Scherrer equation from the broadening of the diffraction peak. The Scherrer equation is given as follows [37]:

$$t_{hkl} = \frac{K\lambda}{\beta_{hkl} \cos \theta_{hkl}} \quad (7)$$

where t_{hkl} is the crystal size in the crystallographic directions or defined as the coherence length. K and λ are the Scherrer constant and X-ray wavelength and their values are 0.9 and 1.54 Å, respectively. β_{hkl} is the half-width of the diffraction peak of the Miller indices (hkl) and θ_{hkl} is the Bragg angle. In order to carry out the calculation, the individual peak caused by the different crystal form of PEN must be resolved first. The X-ray diffraction curves of pure PEN and the 30:70 P64/PEN blend were deconvoluted into five and six components, respectively, by approximating peaks

Table 3

The coherence lengths of the P64/PEN blends in the (100), (010) and $(\bar{1}\bar{1}0)$ planes

P64/PEN	(100)		(010)		$(\bar{1}\bar{1}0)$	
	$\beta_{(100)}^a$	$t_{(100)}$ (nm)	$\beta_{(010)}^a$	$t_{(010)}$ (nm)	$\beta_{(\bar{1}\bar{1}0)}^a$	$t_{(\bar{1}\bar{1}0)}$ (nm)
0:100	1.05	7.9	1.32	6.6	1.54	5.8
3:97	0.99	8.3	1.11	7.8	1.29	6.9
6:94	1.02	8.1	1.21	7.1	1.40	6.4
12:88	1.22	6.8	1.62	5.3	2.12	4.2
30:70	1.45	5.7	2.4	3.6	2.96	3.0

^a The half-width of the diffraction peak of the Miller indices (hkl) in degrees.

with Gaussian curves as shown in Fig. 7(a) and (b). Since the crystallization of P64 become dominant when the amount of P64 is more than 50%, we only estimated the crystal sizes of the pure PEN and P64/PEN blends with P64 as the minor components. In Table 3, the coherence lengths $t_{(100)}$, $t_{(010)}$ and $t_{(\bar{1}\bar{1}0)}$ of the pure PEN were 7.9, 6.6 and 5.8 nm, respectively. For the 3:97 and 6:94 P64/PEN blends, the $t_{(100)}$, $t_{(010)}$ and $t_{(\bar{1}\bar{1}0)}$ are larger than that of pure PEN. As the amount of P64 is equal to or larger than 12% in the blend, the coherence lengths decreased with the P64 content, as given in Table 3. From these results, we can conclude that the PEN crystals in the P64/PEN blends with low P64 content appeared to be more regular than that of the pure PEN. This phenomenon is similar to that of the PBT/LCP blend [38].

The polarized micrographs of PEN, P64 and P64/PEN blends are shown in Fig. 8. In Fig. 8(a), the pure P64 exhibited strong birefringence. The dark region and the light region represented the amorphous phase and the crystalline phase of PEN, respectively, as shown in Fig. 8(b), and the spherulites in the light region had a mean size about 2 μm . In the cases of the 3:97 and 6:94 P64/PEN blends, the sizes of spherulites are 3.5 and 2.5 μm , respectively, which are greater than that of pure PEN, as shown in Fig. 8(c) and (d). When the amount of P64 increased to 12%, the size of the spherulite became smaller than that of pure PEN as shown in Fig. 8(e). For the 30:70 P64/PEN blend, the light region actually contained both the birefringence of P64 and the crystalline phase of PEN, as shown in Fig. 8(f). The close coexistence of these two phases revealed that there was no strong phase separation present for P64 and PEN at this composition. When the amount of P64 increased to 50% and then to 70%, the birefringence of P64 became more intensive as shown in Fig. 8(g) and (h).

4. Conclusions

The amorphous phases in blends of random liquid crystalline copoly(oxybenzoate-ethylene terephthalate) (P64) and semicrystalline poly(ethylene-2,6-naphthalene dicarboxylate) (PEN) were found to be miscible as evidenced by a

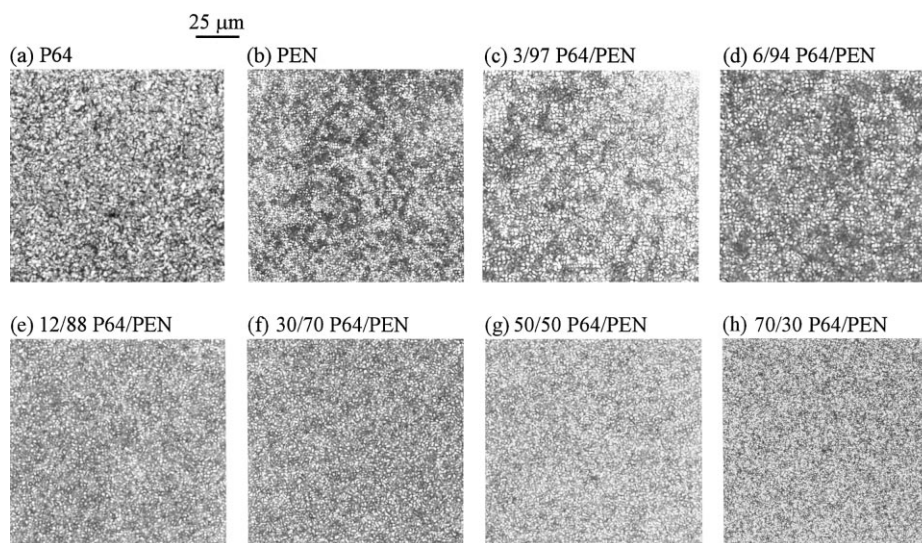


Fig. 8. The room-temperature birefringence pictures of pure polymers and the P64/PEN blends after annealing at 200°C for 4 h: (a) P64; (b) PEN; (c) 3/97 P64/PEN; (d) 6/94 P64/PEN; (e) 12/88 P64/PEN; (f) 30/70 P64/PEN; (g) 50/50 P64/PEN; (h) 70/30 P64/PEN.

composition-dependent single T_g . The composition-dependent T_g can be predicted by the Gordon–Taylor equation with $k = 0.30$. Moreover, the P64/PEN blends were confirmed to be thermodynamically miscible at the melt state by having a Flory–Huggins interaction parameter, χ_{12} , of -1.13 , through the equilibrium melting-depression analysis. The coherence length of PEN in the P64/PEN blends was larger than that of pure PEN when a small amount of P64, around 3%, was present, indicating that the regularity of PEN crystals in the blends was more perfect than that of pure PEN.

Acknowledgements

The authors appreciate the financial support provided by the National Science Council through Project NSC88-2216-E-009-008.

References

- [1] Kiss G. *Polym Engng Sci* 1987;27:410.
- [2] Kolhi A, Chung N, Weiss RA. *Polym Engng Sci* 1989;29:573.
- [3] Brostow W. *Polymer* 1990;31:979.
- [4] Wei KH, Kiss G. *Polym Engng Sci* 1996;36:713.
- [5] Wei KH, Hwang WJ, Tyan HL. *Polymer* 1996;37:2087.
- [6] Wei KH, Jang HC, Ho JC. *Polymer* 1997;38:3521.
- [7] Wei KH, Ho JC. *Macromolecules* 1997;30:1587.
- [8] Wei KH, Tyan HL. *Polymer* 1998;39:2103.
- [9] Kimura M, Porter RS. *J Polym Sci, Polym Phys Ed* 1983;21:367.
- [10] Laivins GV. *Macromolecules* 1989;29:3974.
- [11] Nakai A, Shiwaku T, Wang W, Hasegawa H, Hashimoto T. *Macromolecules* 1996;29:2259.
- [12] Nakai A, Wang W, Ogasawa S, Hasegawa H, Hashimoto T. *Macromolecules* 1998;31:5391.
- [13] Meng YZ, Tjong SC. *Polymer* 1998;39:99.
- [14] Ishiharada M, Hayashi S, Saito S. *Polymer* 1989;30:349.
- [15] Murakami S, Nishikawa Y, Tsuji M, Kawaguchi A, Kohjiya S, Cakmak M. *Polymer* 1995;36:291.
- [16] Zhang H, Ward IM. *Macromolecules* 1995;28:7622.
- [17] Mencik Z. *Chem Prum* 1976;17(2):78.
- [18] Zachmann HG, Wiswe D, Gehrke R, Riekel C. *Makromol Chem Suppl* 1985;12:175.
- [19] Kim SJ, Nam JY, Lee YM, Im SS. *Polymer* 1999;40:5623.
- [20] Nicely VA, Dougherty JT, Renfro LW. *Macromolecules* 1987;20:578.
- [21] Ho JC, Lin YS, Wei KH. *Polymer* 1999;40:3843.
- [22] Fox TG. *Bull Am Phys Soc* 1956;1:123.
- [23] Gordon M, Taylor J. *J Appl Chem* 1952;2:493.
- [24] Kimura M, Porter RS. *J Polym Sci, Polym Phys Ed* 1983;21:367.
- [25] Xing P, Ai X, Dong L, Feng Z. *Macromolecules* 1998;31:6898.
- [26] Hoffman JD, Weeks JJ. *J Res Natl Bur Stand* 1962;66:13.
- [27] Boyd R. *Polymer* 1985;26:323.
- [28] Boyd R. *Polymer* 1985;26:1123.
- [29] Marand H, Xu J, Srinivas S. *Macromolecules* 1998;31:8219.
- [30] Canadas JC, Diego JA, Mudarra M, Belana J, Diaz-Calleja R, Sanchis MJ, Jaimés C. *Polymer* 1999;40:1181.
- [31] Aoki Y, Li L, Amari T, Nishimura K, Arashiro Y. *Macromolecules* 1999;32:1923.
- [32] Nabi Saheb D, Jog JP. *J Polym Sci, Polym Phys Ed* 1999;37:2439.
- [33] Nishi T, Wang TT. *Macromolecules* 1975;8:909.
- [34] Jung HC, Lee HS, Chun YS, Kim SB, Kim WN. *Polym Bull* 1998;41:387.
- [35] Bicakci S, Cakmak M. *Polymer* 1998;39:4001.
- [36] Cheng SZD, Wunderlich B. *Macromolecules* 1988;21:789.
- [37] Cullity BD. *Elements of X-ray diffraction*. 2nd ed. Reading, MA: Addison-Wesley, 1978 (p. 102).
- [38] Yan H, Xu J, Mai K, Zeng H. *Polymer* 1999;40:4865.