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Thermal properties of blends of a thermotropic liquid crystalline copolyester of poly(hydroxy benzoic acid-*co*-ethylene terephthalate) and polyarylate

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Summary

Thermal properties and transesterification reaction of blends of polyarylate (PAr) and a thermotropic liquid crystalline polymer (LCP) were investigated by differential scanning calorimetry (DSC) and Fourier Transform infrared (FT-IR) spectroscopy. In the thermogram of PAr-LCP blends, two glass transition temperatures (T_gs) were observed. Phase behavior of the blends revealed that the LCP dissolved more in the PAr-rich phase than did the PAr in the LCP-rich phase, indicating partial miscibility between two polymers. The polymer-polymer interaction parameter (χ_{12}) was calculated, and ranged from 0.069 to 0.076. In the calculation of the χ_{12}, the anisotropy of the LCP was considered. After annealing, the two T_gs of the blends were shifted toward the center. In the FT-IR spectroscopy study of the annealed PAr-LCP blends, three new characteristic peaks of the ester group were detected. The DSC and FT-IR results suggested that transesterification reaction between PAr and LCP occurred under the annealed condition.

Introduction

In recent year, many areas of research related to the development of new and improved commercial products from liquid crystalline polymer (LCP) and LCP blends have been studied (1-13). Because LCP has an orientation in microscopic scale, when it was blended with other engineering polymers, thermotropic liquid crystalline polymer could contribute to the physical properties of the blends. In particular, main chain thermotoropic liquid crystalline polymer, which feature anisotropic melts within a given temperature range, have considerable attention due to their low melt viscosity and ease of melt processability in the liquid crystalline state (3-6).

Polyarylate (PAr) is a kind of aromatic polyesters, except a special case, the most commercial PAr is an amorphous thermoplastics that combine clarity, high heat-deflection temperature, high impact strength and good electrical properties with inherent ultraviolet stability and flame resistance (14,15). But it has a difficulty to process for its high glass transition temperature (T_g), therefore LCP was introduced which can play the role of decreasing viscosity and make an easy to process (5,16).

PAr-LCP blends have good mechanical properties and are used to the places required high performance (14). However, thermodynamic properties such as polymer-polymer interaction

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parameter (χ_{12}) of the PAr and LCP blends were not reported in the melted or solution state yet.

Hong and coworkers (14) reported that PAr is partially miscible with LCP (Vectra A950) and the transesterification did not occur when these were extruded at 613 K. In order to improve compatibility, transesterification can be used in immiscible polymer blends system (17-24). This reaction can be observed by the torque measurement of the screw extruder, change of glass transition temperature (T_gs), nature of the adhesive bonding by secondary ion mass spectrometry profile, and presence ester peak in NMR or FT-IR (17-24).

In our earlier studies (1,2), we reported the blends of liquid crystalline polymer with polycarbonate, polyether imide, and poly(ether ether ketone). In the present study, we examine thermal properties and transesterification reactions of screw-extruded PAr-LCP blends by DSC and FT-IR. Also, using the Flory's lattice theory (1,2,25,26), we are examining the degree of disorder (y/x_1) and polymer-polymer interaction parameter (χ_{12}) between PAr and LCP.

Experimental

Polymers

The polymers used in this work were obtained from commercial sources. Polyarylate (PAr) was used Ardel D-100 and was provided by Amoco Corporation. It is a copolymer of bisphenol A with a mixture of terephtalic/isophtalic acids at a proportion of 50/50. Thermotropic liquid crystalline polymer (LCP) designated as Rodrun-5000, which was produced by Unitika Corporation was random copolyester containing 20 mol% poly(ethylene terephthalate) (PET) and 80 mol% *p*-hydroxy benzoic acid (PHB). Since the homopolymer of PHB shows two prominent melting transitions at very high temperatures: the first at 613-623 K and the second at 713-723 K (27), the copolymer of PET and PHB was used in this study. The characteristics of polymer samples used in this work are shown in Table 1.

Blend Preparation

Polymer blends were prepared using a 20 mm diameter laboratory scale screw extruder, with a 24:1 length to diameter screw. The extruder was set at 583 K in the barrel zones

Table 1. Characterization of polymer sample used in the PAr-LCP blends

	$\overline{M_w}$	$\overline{M_n}$	T_g(K) [a]	T_m(K) [a]	ΔC_p(J g^{-1} k^{-1}) [a]	ρ(g cm^{-3}) [b]
PAr[c]	45,800[d]	18,400[d]	468.0	-	0.151	1.16
LCP[e]	-	19,500[f]	343.1	554.6	0.036	1.41

[a] Measured in our laboratory using DSC.
[b] Measured in our laboratory using specific gravity chain balance.
[c] Supplied by Amoco Co.
[d] Measured by GPC.
[e] Supplied by Unitika Co.
[f] Data from ref. (28).

and die was kept at 513 K. Pellet of the two polymers were mixed to the desired composition and dried at 393 K for 24 hr before use to ensure removal of any moisture absorbed.

Differential Scanning Calorimetry Measurements

The thermal properties of all samples were measured calorimetrically using a Perkin Elemer DSC7. The PAr-LCP blend samples were initially heated from 298 K to 583 K at a heating rate of 20 K min^{-1} and cooled with a cooling rate of 320 K min^{-1}. Several cycles of heating and cooling were performed to observe the glass transition of the component polymers more clearly. To observe transesterification reaction between the PAr and LCP, the blend samples were annealed at 583 K from 3 to 60 min in DSC.

Fourier Transform infrared (FT-IR) spectroscopy

The FT-IR was used to investigate the chemical interaction that could occur between the two phases with a Perkin Elemer Fourier Transform infrared FT-IR spectroscopy, spectrum 2000, at a resoultion 2 cm^{-1}.

Results and discussion

Glass Transition Temperatures (T_gs) of the Blends

In Figure 1, the glass transition temperatures (T_gs) of the PAr-LCP blends are shown. From Figure 1, we can see two T_gs of PAr-LCP blends, which we designate as T_g(PAr), associate with the PAr-rich phase and T_g(LCP), associate with the LCP-rich phase. The T_g(PAr) decreases 12-16 K with blend composition and T_g(LCP) increases 1-2 K with LCP weight fraction. Thus, the decrease in T_g(PAr) is more pronounced than that of T_g(LCP).

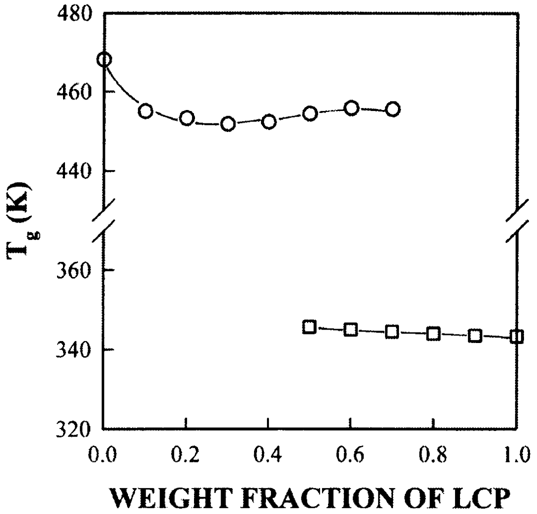

Fig. 1. Effect of blend composition on the T_g (PAr) (O) and T_g(LCP) (□) in the PAr-LCP blends.

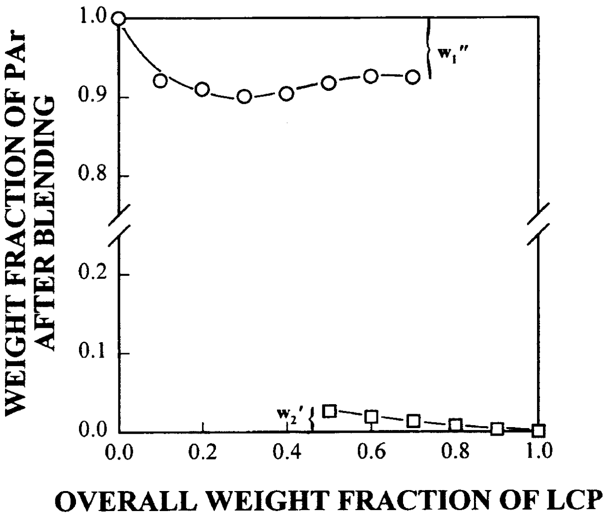

Fig. 2. Phase composition diagram of PAr-LCP blends: (O) weight fraction of PAr in the PAr rich phase; (□) weight fraction of PAr in the LCP-rich phase

From the glass transition temperature of the blends, we can estimate the apparent weight fractions of LCP in the LCP-rich phase and PAr in the PAr-rich phase by Fox equation (29) as reported by Kim and Burns (30-32). The Fox equation may be rearranged to eq 1 where w_1' is the apparent weight fraction of polymer 1 in the polymer 1-rich phase and $T_{g1,b}$ is the observed T_g of polymer 1 in the blends, and T_{g1} and T_{g2} are the T_gs of pure polymer 1 and 2, respectively.

$$w_1' = \frac{T_{g1}(T_{g1,b} - T_{g2})}{T_{g1,b}(T_{g1} - T_{g2})} \tag{1}$$

Applying eq 1 to the DSC results of T_gs in the blends, we have calculated the apparent weight fraction of LCP in the LCP-rich phase (w_1') and apparent weight fraction of PAr in the PAr-rich phase (w_2''), which are presented in Figure 2 and Table 2. From Figure 2, we can see that the LCP dissolved more in the PAr-rich phase (w_1'') than does the PAr in the LCP-rich phase (w_2'). In the study of blend of LCP with poly(ethylene terephthalate) by NMR, Tang et al. (33) observed that the LCP can penetrate PET regions in blends upon annealing in the melt. In our earlier studies (1,2) for the blends of LCP with polycarbonate (PC), polyetherimide (PEI), and poly(ether ether ketone) (PEEK), similar behavior was observed that the LCP dissolved more in the PC-, PEI-, and PEEK- rich phases than did the PC, PEI, and PEEK in the LCP-rich phase. Using the apparent weight fractions that we have calculated from the glass transition temperatures of the blends, we can then estimate the polymer-polymer interaction parameter (χ_{12}).

Polymer-Polymer Interaction Parameter (χ_{12})

From the experimentally determined compositions in each phase of the PAr-LCP blends, we can determine the polymer-polymer interaction parameter (χ_{12}) between the component polymers, provided that the systems are at equilibrium or nearly so. The polymer-polymer interaction parameter (χ_{12}) and the degree of disorder (y/x_1) can be determined by the equations which was reported in our earlier studies (1,2).

When the anisotropy of LCP is not considered, the Flory-Huggins polymer-polymer

Table 2. Polymer-polymer interaction parameter (χ_{12}) and degree of disorder (y/x_1) between PAr and LCP in the PAr-LCP blends

Blend[a]	$w_1'^{\,b}$	$w_2''^{\,b}$	$v_1'^{\,b}$	$v_2''^{\,b}$	$(y/x_1)^c$	$\chi_{12}^{\,c}$	$\chi_{12}^{\,d}$
0.5	0.9742	0.0829	0.9688	0.9308	0.91	0.069	0.070
0.6	0.9814	0.0742	0.9775	0.9381	0.89	0.073	0.073
0.7	0.9868	0.0757	0.9840	0.9369	0.87	0.073	0.076

[a] Blend composition given as overall weight fraction of LCP in the PAr-LCP blend.

[b] Single prime and double prime denote LCP-rich phase and PAr-rich phase, respectively; subscript 1 and 2 denote LCP and PAr component, respectively: $w_2' = 1 - w_1'$ and w_2''.$= 1 - w_1''$ · Volume fraction (v) are obtained from weight fractions (w) divided by densities of each polymer.

[c] All values were calculated from the equations which considered the anisotropy of LCP (1).

[d] All values were calculated from the equation which neglected the anisotropy of LCP (32).

interaction parameter (χ_{12}) can be determined by the following eq 2 which was reported by Kim and Burns (30-32).

$$\chi_{12} = \frac{\{(\phi_1'^2-\phi_1''^2)[m_2 \ln(\phi_1''/\phi_1')+(m_1-m_2)(\phi_2'-\phi_2'') + (\phi_2'^2-\phi_2''^2)[m_1 \ln(\phi_2''/\phi_2')+(m_2-m_1)(\phi_1'-\phi_1'')]\}}{2m_1m_2(\phi_1'^2-\phi_1''^2)(\phi_2'^2-\phi_2''^2)} \qquad (2)$$

where m_1 and m_2 are constants related to the degree of polymerization LCP and flexible polymer.

In Table 2, we can see the value of the polymer-polymer interaction parameter (χ_{12}) and degree of disorder (y/x_1) in PAr-LCP blends. Values of x_{1m} = 44.6 and x_2 = 51.3 were used for LCP and PAr, respectively. In Table 2, we can also find that the χ_{12} of PAr-LCP blends have almost the same value whether the anisotropy of LCP is considered or not. This result may come from that the degree of order (y/x_1) of the LCP in the PAr-LCP blends is large which is approaching to almost a unit value in the blends.

Transesterification between PAr and LCP

During the melt processing, there is a possibility of transesterification between ester group of PAr and LCP (17-24). These transesterification reaction in polyester blends lead initially to block copolymers and finally to a random copolymer, since all repeat bond linkages of a given structural unit are equally likely to react. The relative population of homopolymer and block copolymers depends on the transesterifying will depend on the level of the exchange reaction produced, and this should be more evident in incompatible or partially compatible polymer mixtures (16,28). To investigate the possibility of the transesterification in PAr-LCP blends, T_gs of the PAr-LCP blends were examined by DSC.

In Figure 3, we can see that T_gs of the PAr in the PAr-LCP blends decrease with a increasing annealing time at 583 K. This result may be an indication that a copolymer formed by an ester interchange reaction made a role to increase miscibility in the blends. The T_g(PAr) and T_g(LCP) are shown in Figure 4, when the PAr-LCP blends are annealed at 583 K for 30 min. The T_g(PAr) of annealed PAr-LCP blends decreases 13-26 K and the T_g(LCP) of annealed blends increases about 2-9 K with blend composition. From the DSC data, it is suggested that the ester interchange reaction between PAr and LCP can occur at high temperature and longer annealing time with blend composition. During the development of transesterification reaction we may expect a change to occur in physical properties due to the newly formed structure, and many researcher proposed to detect this chemical change by variety experimental tool (17-24).

Figure 5 (a)-(e) show the FT-IR spectrum of 10/0, 7/3, 5/5, 3/7, and 0/10 PAr-LCP blends annealed at 583 K and 800 psi for 30 min. From Figure 5 (c) and (d), we can observe three new peaks of the ester group at 1233, 1189, and 1147 cm^{-1} after annealing. It is indicated that the appearance of three new peaks are not simply caused by hydrogen bond but can caused by some kind of chemical reaction like a transesterification at a given annealing condition.

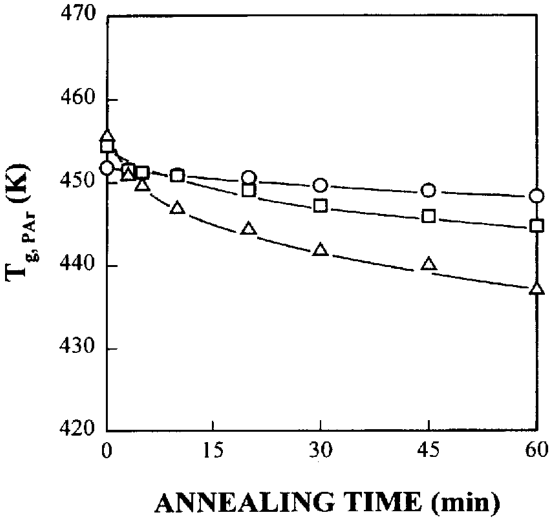

Fig. 3. Effect of annealing time on the T_g of PAr in the PAr-LCP blends annealed in DSC at 583 K: PAr-LCP 7/3(○), 5/5(□), and 3/7(△).

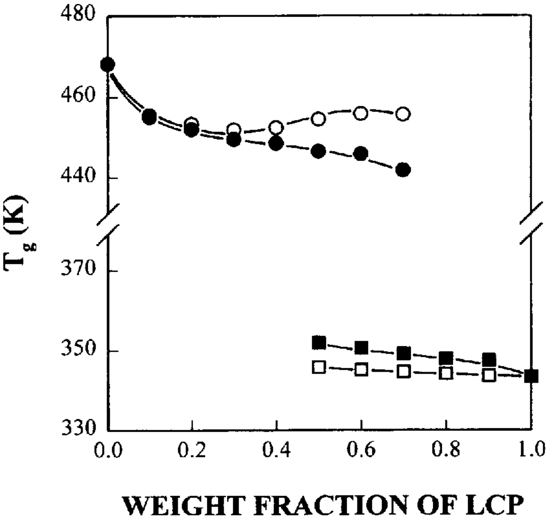

Fig. 4. Effect of blend composition on the T_g of PAr (○,●) and T_g of LCP (□,■) in the PAr-LCP blends: unannealed (○,□) annealed at 583 K for 30 min (●,■).

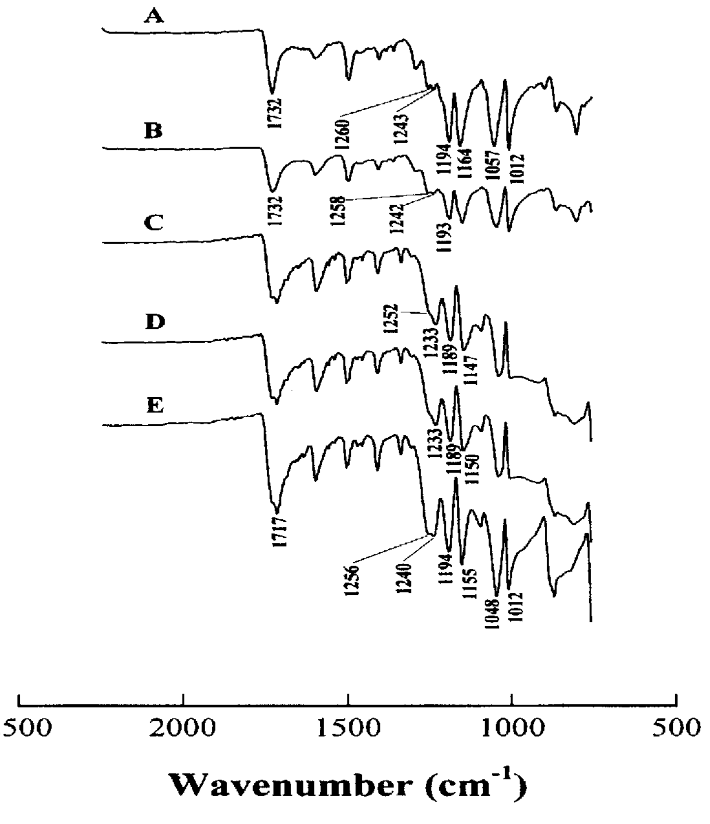

Fig. 5. FT-IR spectra of the PAr-LCP blends annealed at 583 K and 800 psi for 30 min : PAr-LCP (a) 10/0, (b) 7/3, (c) 5/5, (d) 3/7, and (e) 0/10.

Conclusions

From the DSC thermogram data, we can see two glass transition temperatures (T_gs) of the PAr-LCP blends, which we designate as T_g(PAr), associate with the PAr-rich phase and T_g(LCP), associate with the LCP-rich phase. The T_g(PAr) decreases 12-16 K and T_g(LCP) increases 1-2 K with blend composition. Therefore, the decrease in T_g(PAr) is more pronounced than the increase of T_g(LCP) in the PAr-LCP blends. From the DSC results, it is concluded that the LCP dissolved more in the PAr-rich phase than did the PAr in the LCP-rich phase. The polymer-polymer interaction parameter (χ_{12}) of the PAr-LCP blends has been calculated and found to be from 0.069 to 0.076.

The T_g(PAr) of annealed PAr-LCP blends decreases 13-26 K and the T_g(LCP) of annealed blends increases about 2-9 K with blend composition. From the FT-IR results of the PAr-LCP blends, three new peaks of the ester group were observed at 1233, 1189, and 1147 cm^{-1} after annealing. From the DSC data and FT-IR results, it is suggested that transesterification reaction between PAr and LCP occurred under the annealed condition.

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References

(1) Lee HS, Jung WH, Kim WN (1996) Polym. Bull. 37: 503
(2) Jung HC, Lee HS,Chun YS, Kim S-B, Kim WN (1998) Polym. Bull. 41:387
(3) Lee HS, Denn MM (1999) J. Rheol. 43:1583
(4) Kim WN, Denn MM (1992) J. Rheol 36:1477
(5) Blizard KG, Baird DG (1987) Polym. Eng. Sci. 27: 653
(6) Kiss G (1987) Polym. Eng. Sci. 27: 410
(7) Lee HS, Jung WH, Jung HW, Kim WN, Hyun JC (1996) Polymer(Korea) 20:813
(8) Hurduc N, Daoudi A, Buisine JM, Barboiu V, Simionescus CI, (1997) Eur. Polym. J. 34:123
(9) He JS, Liu J (1999) Polymer 40:959
(10) Dreezen G, Koch MHJ, Reynaers H, Groeninckx G (1999) Polymer 40:6451
(11) Weiss RA, Ghebremeskel Y, Charbonneau L (2000) Polymer 41:3471
(12) Carpaneto L, Lesage G, Pisino R, Trefiletti V (1999) Polymer 40:1781
(13) Ellis TS (1998) Polymer 39:4741
(14) Hong SM, Kim BC, Whang SS, Kim KU (1993) Polym. Eng. Sci. 33: 630
(15) Ahn TO, Lee SM (1993) Polymer 34: 4156
(16) Golovoy A, Cheung MF (1989) Polym. Eng. Sci. 29: 85
(17) Porter RS, Wang LH (1992) Polymer 33: 2019
(18) Kotliar AM (1981) J. Polym. Sci., Macromol. Rev. 16: 367
(19) Miley DM, Runt J (1992) Polymer 33: 4643
(20) Mondragon I, Nazabal J (1986) J. Appl. Polym. Sci. 32: 6191
(21) Porter RS, Zonza JM, Kimura M, Desper CR, George ER (1989) Polym. Eng. Sci. 29: 55
(22) Oh TS, Ryou JH, Chun YS, Kim WN (1997) Polym. Eng. Sci. 37: 838

(23) Wei KH, Ho JC (1997) Macromolecules 30:1587
(24) Frich D, Hall A, Economy J (1998) Macromol. Chem. Phys. 199:913
(25) Flory PJ (1978) Macromolecules 11:1141
(26) Flory PJ, Ronca G (1979) Mol. Cryst. Liq. Cryst. 54:311
(27) Mühlebach A, Economy J, Johnson RD, Karis T, Lyerla J (1990) Macromolecules 23:1803
(28) Friedrich K, Hess M, Kosfeld R (1988) Makromol. Chem., Makromol. Symp. 16: 251
(29) Fox TG (1956) Bull. Am. Phys. Soc. 1: 123
(30) Kim WN, Burns CM (1987) Macromolecules 20:1876
(31) Kim WN, Burns CM (1987) J. Appl. Polym. Sci. 34: 945
(32) Kim WN, Burns CM (1989) J. Polym. Sci., Polym. Phys. 28: 409
(33) Tang P, Reimer JA, Denn MM (1993) Macromolecules 26: 4269