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Blends of a thermotropic liquid crystalline polymer and some flexible chain polymers and the determination of the polymer-polymer interaction parameter of the two polymers

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Summary

Blends of a thermotropic liquid crystalline polymer (LCP) with poly(ether imide) (PEI), poly(ether ether ketone) (PEEK), polysulfone (PSF) and polyarylsulfone (PAS) prepared by screw extrusion have been investigated by differential scanning calorimeter and dynamic mechanical thermal analysis. From the measured glass transition temperature (T_g) and specific heat increment (ΔC_p) at the T_g, it appears that the LCP dissolves more in the PEI- and PEEK-rich phases than does the PEI and PEEK in the LCP-rich phase. From the DSC study of PSF-LCP and PAS-LCP blends, the T_g(PSF) and T_g(PAS) of each blends are almost constant with blend composition. Therefore, it is concluded that PSF and PAS are immiscible with LCP. The polymer-polymer interaction parameter (χ_{12}) and the degree of disorder (y/x_1) of LCP have been investigated using the Flory lattice theory in which the anisotropy of LCP is considered. The χ_{12} values have been calculated from the T_g data and found to be 0.181 ± 0.004 at 593 K for the PEI-LCP blends and 0.069 ± 0.006 at 623 K for the PEEK-LCP blends. Using the previously presented method, the χ_{12} and y/x_1 in partially miscible systems have been determined.

Introduction

The blends of a flexible chain polymer with a thermotropic liquid crystalline polymer (LCP) have been of great interest in recent year (1-15). Some investigators(4,13) have used the thermal properties such as glass transition temperature (T_g) and specific heat increment (ΔC_p) at T_g to investigate the polymer-polymer compatibility between a thermotropic LCP and a flexible chain polymer by differential scanning calorimetry (DSC). The polymer blends which have been reported have contained polycarbonate (PC) (1-5), poly(ether imide) (PEI) (6-9), poly(ether ether ketone) (10-13), and polysulfone (PSF) (14,15).

Friedlich and coworkers (4) have reported that a thermotropic LCP is partially miscible with polycarbonate (PC). Bafna and coworkers (9) have studied the blends of a thermotropic LCP and poly(ether imide) (PEI) using thermal analysis and scanning electron microscopy (SEM). They have reported that PEI is partially miscible with the themotropic LCP. Acierno and Naddeo (12) have reported that a thermotropic LCP is miscible with PEEK by using thermal analysis. Bretas and Baird (13) have reported that a

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thermotropic LCP is partially miscible with poly(ether ether ketone) (PEEK) by using thermal analysis. Golovoy and coworkers (15) have reported that a thermotropic LCP is immiscible with PSF by thermal analysis. In our previous work (1), we have applied the lattice theory to the blend of polycarbonate and a thermotropic liquid crystalline polymer and reported the equilibrium degree of disorder (y/x_1) and polymer-polymer interaction parameter (χ_{12}) of the blend at melt processing temperature.

In our present study, we examine the thermal properties of screw-extruded blends of a thermotropic LCP with poly(ether imide) (PEI), poly(ether ether ketone) (PEEK), polysulfone (PSF) and polyarylsulfone (PAS) by thermal analysis. The miscibility between a thermotropic LCP and a flexible chain polymer at melt processing temperature is quite an important factor in order to understand the physical properties of the blend. Using the lattice theory (1), we determine the degree of disorder (y/x_1) and the polymer-polymer interaction paremeter (χ_{12}) between the component polymers at melt processing temperature for the PEI-LCP, PEEK-LCP, PSF-LCP, and PAS-LCP blends. Also, a method is presented to determine the χ_{12} and y/x_1 in partially miscible systems by using the experimentally determined glass transition temperature.

Experimental

Polymers.

The polymers used in this work were obtained from commercial sources. The characteristics of polymer samples used in this work are shown in Table 1. The glass transition temperature (T_g) and specific heat increment (ΔC_p) at T_g were measured by differential scanning calorimetry (DSC), using procedures reported earlier (1).

Thermotropic liquid crystalline polymer (LCP) designated as Rodrun-5000, which was

Table 1. Characteristics of polymer used in this work

	$\overline{M_w}$	$\overline{M_n}$	T_m(K) [a]	T_g(K) [a]	ΔC_p($J\ g^{-1}\ K^{-1}$) [a]	ρ($g\ cm^{-3}$) [b]
Rodrun-5000[c]	-	19,500[d]	554.9	343.4	0.036	1.41
Rodrun-3000[c]	-	21,500[d]	474.2	331.6	0.052	1.40
PEI[e]	-	12,000[f]	-	492.1	0.241	1.27
PEEK[g]	39,400[f]	14,000[f]	611.5	419.2	0.308	1.26
PSF[h]	50,000[i]	22,400[I]	-	463.9	0.235	1.23
PAS[h]	-	-	-	495.0	0.227	1.32
PC[j]	22,800[k]	9,760[k]	-	424.4	0.231	1.20

[a] Measured in our laboratory using DSC.

[b] Measured in our laboratory using specific gravity chain balance.

[c] Supplied by Unitika Co.

[d] Data from ref. 4.

[e] Supplied by Gerneral Electrics Co. designated as Ultem 1000

[f] Data from ref. 16.

[g] Supplied by ICI Co.

[h] Supplied by Amoco Co.

[i] Data from ref. 15.

[J] Supplied by Sam Yang Kasei Co.

[K] Data from supplier.

produced by Unitika Co., was random copolyester containing 20 mol% poly(ethylene terephthalate) (PET) and 80 mol% *p*-hydroxy benzoic acid (PHB).

Blend Preparations.

To prepare melt blends, the polymer samples were dried in a vacuum oven at 120 °C for 24 hr. Blends were prepared using a 20 mm. diameter laboratory scale screw extruder, with a 24:1 length to diameter screw. The temperature of the extruder were maintained at 593, 623, 572, and 572 K in the barrel zones for the PEI-LCP, PEEK-LCP, PSF-LCP, and PAS-LCP blends, respectively. The Rodrun-5000 was used as a LCP component for the PEI-LCP, PEEK-LCP, PSF-LCP, and PAS-LCP blends. The Rodrun-3000 was used as a LCP component for the PC-LCP blends (1).

Differential Scanning Calorimetry Measurements.

The thermal properties of all samples were measured calorimetrically using a Perkin-Elemer DSC7. The PEI-, PSF-, and PAS-LCP blends samples were initially heated from 293 K to 593 K at a heating rate of 20 K/min and cooled with a cooling rate of 320 K/min. Several cycles of heating and cooling were performed to observe the glass transition of the component polymers more clearly. The PEEK-LCP blend samples were initially heated from 293 K to 623 K at a heating rate of 20 K/min and hold one minute and the samples at 623 K were then quenched in liquid nitrogen. Finally, the PEEK-LCP blend samples were heated with a heating rate of 20 K/min. Dynamic mechanical thermal analysis was done on a Polymer Laboratories model MK III in bending mode.

Results and discussion

Glass Transition Temperatures (T_gs) of the Blends.

In Figure 1, the DSC thermograms of the PEI-LCP blends are shown. From Figure 1, the T_g(PEI) of the blends is decreased 4 - 8 K with blend composition. In Figure 2, we have investigated the T_gs of the PEI-LCP blends using the dynamic mechanical thermal analysis. From this Figure, we have observed two peaks which are shown that the upper peak is associate with the T_g(PEI) and the lower peak is associated with the T_g(LCP). The results shown in Figure 2 are consistent with the results shown in Figure 1 by DSC for the PEI-LCP blends.

In Figures 3 and 4, we can see the two T_gs for the various compositions of the blends of a thermotropic LCP with PEI, PEEK, PSF, PAS, and PC. The DSC results of the PC-LCP blends are the previous work published in our laboratory (1), and shown just for comparision with other blends. For the PEEK-LCP blends, the samples have been quenched in the liquid nitrogen at the melted state before measuring the T_gs of the blends. This was needed in order to minimize the effect of crystallinity of PEEK on the T_gs of the blends. In Figure 3, the T_g of PEI and PEEK is decreased up to 8 K and 4 K with the presence of LCP in the blends, respectively. However, the T_g of PSF and PAS is almost constant with the LCP composition. This result may suggest that the PEI, and PEEK is partially miscible with the LCP but the PSF and PAS is immiscible with the LCP. In Figure 4, the T_g(LCP) in the blends is seen to increase about 2 K with the decrease of the

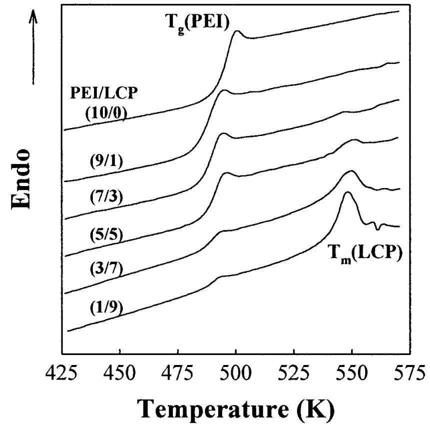

Fig. 1 DSC thermograms for the PEI-LCP blends

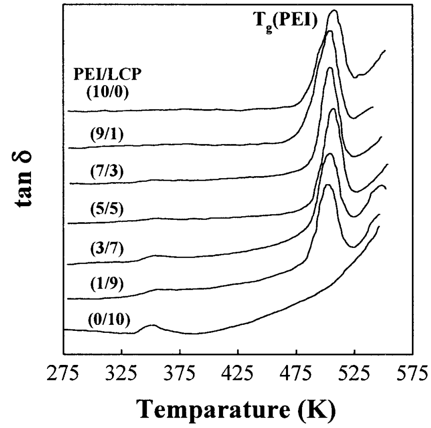

Fig. 2 DMTA results of tan δ for the PEI-LCP blends.

LCP weight fraction. From Figures 3 and 4, we can see that the decrease of T_g(PEI) and T_g(PEEK) is more significant than the increase of the T_g(LCP). From this results, it is suggested that the LCP dissolves more in the PEI- and PEEK-rich phase than does PEI, and PEEK in the LCP-rich phase (1).

From the glass transition temperatures of the blends, we can estimate the apparent weight fractions of LCP in the LCP-rich phase and the PEI- and PEEK-rich phases by Fox equation (17), which is used to predict T_gs for miscible polymer blends. The Fox equation may be rearranged to

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

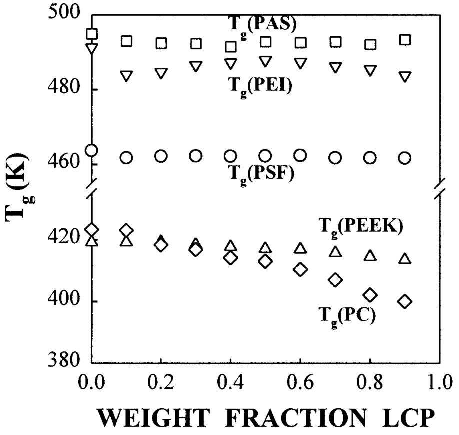

Fig. 3 Effect of blends composition on the T_gs for the blends: (◇) T_g(PC) of the PC-LCP blends; (△) T_g(PEI) of the PEI-LCP blends; (▽) T_g(PEEK) of the PEEK-LCP blends; (○) T_g(PSF) of the PSF-LCP blends; (□) T_g(PAS) of the PAS-LCP blends.

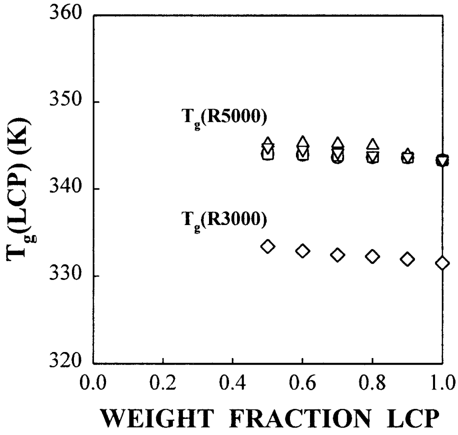

Fig. 4 Effect of blend composition on the T_g(LCP) for the blends: (◇) PC-LCP; (△) PEI-LCP; (▽) PEEK-LCP; (○) PSF-LCP; (□) PAS-LCP.

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. Applying equation 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 the apparent weight fraction of LCP in the PEI-, PEEK-, PSF-, and PAS-rich phases (w_1"). The apparent weight fraction of LCP in each phase of the PEI-LCP blend is presented in Table 2. 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}).

Specific Heat Increment (ΔC_p) at T_g of the Blends.

The values of specific heat increment (ΔC_p) of PEI, PEEK, PSF, PAS, and PC in the blends are presented in Figure 5. In Figure 5, the ΔC_p at T_gs of the phases rich in PEI, PEEK, PSF, PAS, and PC is seen to decrease with the increase of weight fraction of LCP in the blends. For the partially miscible blends, the reduction of the ΔC_p of each component is often reported; the reduction of ΔC_p results from the dissolution of that component in the conjugate phase (1, 18,19). The shift of T_gs and the decrease of ΔC_p of each component shown can be explained by the dissolution of each component in the conjugate phase for a partially miscible system (18). The apparent weight fraction (w) in each phase has been calculated by using equation 1. In Figure 6, the apparent weight fraction of each phase is presented. From this Figure, we can see that the PEI, and PEEK dissolve more in the LCP-rich phase than does the LCP in the PEI- and PEEK-rich phases.

Polymer-Polymer Interaction Parameter (χ_{12})

From the experimentally determined compositions in each phase of the PEI-LCP and PEEK-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

Table 2. Apparent weight fractions (w) and apparent volume fractions (v) of PEI and LCP component in the PEI-rich Phase and LCP-rich Phase.

Blend [a]	$T_{g1,b}$(K)	$T_{g2,b}$(K)	w_2' [b]	w_2'' [b]	v_2' [b]	v_2'' [b]
0.5	344.8	487.9	0.0144	0.9838	0.0160	0.9854
0.6	344.6	487.4	0.0125	0.9814	0.0139	0.9833
0.7	344.3	486.3	0.0096	0.9762	0.0107	0.9785
0.8	343.9	485.5	0.0058	0.9723	0.0064	0.9750
0.9	343.7	483.8	0.0039	0.9640	0.0043	0.9675

[a] Blend composition given as overall weight fraction LCP in the PEI-LCP blends.

[b] Single prime and double prime denote LCP-rich phase and PEI-rich phase, respectively, and subscripts 1 and 2 denote LCP and PEI component, respectively. Weight fractions are calculated from Fox eq; $w_2'=1-w_1'$ and $w_2''=1-w_1''$. Volume fractions (v) are obtained from weight fractions (w) divided by densities of each polymer.

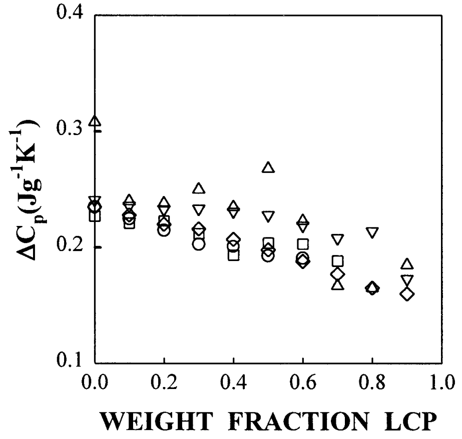

Fig. 5 Specific heat increment (ΔC_p) at the T_g of the blends: (◇) ΔC_p(PC) of the PC-LCP blends; (△) ΔC_p(PEI) of the PEI-LCP blends; (▽) ΔC_p(PEEK) of the PEEK-LCP blends; (○) ΔC_p(PSF) of the PSF-LCP blends; (□) ΔC_p(PAS) of the PAS-LCP blends.

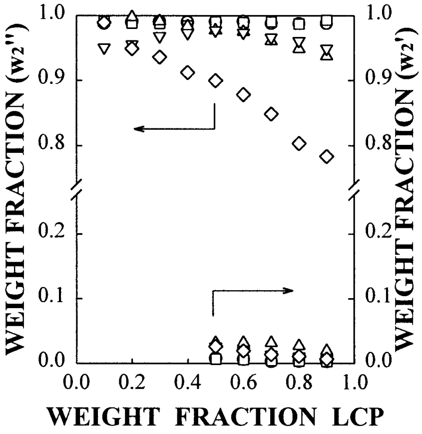

Fig. 6 Apparent weight fractions (w) of the blends: (◇) weight fraction of PC in the PC-LCP blends; (△) weight fraction of PEI in the PEI-LCP blends; (▽) weight fraction of PEEK in the PEEK-LCP blends; (○) weight fraction of PSF in the PSF-LCP blends; (□) weight fraction of PAS in the PAS-LCP blends.

be determined by using the following eqs 2 - 4 those have been derived in the previous papers (1).

$$\exp\left(\frac{-2}{y}\right)=1-v_1\left(1-\frac{y}{x_1}\right) \tag{2}$$

$$\ln\left(\frac{v_1}{v_1''}\right)+v_1\,x_1m\left(\frac{y}{x_1}-\frac{1}{x_1m}\right)-v_1''(x_1m-1)$$
$$+x_1m\left(1-\frac{1}{x_2}\right)(v_2-v_2'')+2m\left[1+\ln\left(\frac{x_1}{y}\right)\right]+x_1m\chi_{12}(v_2^2-v_2^{2}{}'')=0 \tag{3}$$

$$\ln\left(\frac{v_2}{v_2''}\right)+v_1\,x_2\left(\frac{y}{x_1}-\frac{1}{x_1m}\right)-v_1''x_2\left(1-\frac{1}{x_1m}\right)$$
$$+(x_2-1)(v_2-v_2'')+\frac{2x_2}{y}+x_2\chi_{12}(v_1^2-v_1^{2}{}'')=0 \tag{4}$$

where y denotes disorientation, (m+1) is the number of flexible joints in a LCP molecules, x_1 is the axis ratio of each m rods comprising the molecule, x_2 is the contour length of flexible chain polymer, χ_{12} is the polymer-polymer interaction parameter, v_1' is the apparent volume fraction of component 1 in the component 1-rich phase, and v_1'' is the apparent volume fraction of component 1 in the component 2-rich phase. When the anisotropy of LCP is not considered, the Flory-Huggins polymer-polymer interaction parameter (χ_{12}) can be determined by using the following eq 5 as reported by Kim and Burns (18).

$$\chi_{12} = \frac{\begin{array}{l}\{(\phi_1'^2-\phi_1''^2)[m_2 \ln(\phi_1''/\phi_1') + (m_1 - m_2)(\phi_2'-\phi_2'')\\ +(\phi_2'^2-\phi_2''^2)[m_1 \ln(\phi_2''/\phi_2') + (m_2 - m_1)(\phi_1'-\phi_1'')]\}\end{array}}{2m_1 m_2(\phi_1'^2-\phi_1''^2)(\phi_2'^2-\phi_2''^2)} \qquad (5)$$

In calculations, the contour length (x_2) of flexible polymers and the total length of LCP (x_1m) were determined by the following relation (18).

$$\frac{x_1 m}{x_2} = \frac{\overline{M_{n1}}/\rho_1}{\overline{M_{n2}}/\rho_2} = \frac{V_1}{V_2} \qquad (6)$$

Where $\overline{M_n}$ is the number-averaged molecular weight and ρ is the density of the polymer. V_1 and V_2 are the molar volume of LCP and flexible polymer, respectively. The choice of a lattice site volume can be rather arbitrary, but once a site volume has been chosen for one of the components, it must be the same for the other component. Here, a repeating unit of flexible polymer is chosen as a lattice site volume.

In Table 3, the values of the polymer-polymer interaction parameter (χ_{12}) and degree of disorder (y/x_1) are compared for the PEI-LCP and PEEK-LCP blends. We have calculated the χ_{12} and y/x_1 from measured volume fractions for the PEI-LCP and PEEK-LCP blends. The volume fraction was obtained from weight fraction divided by densities of each polymer. Values of $x_1m = 30.1$ and $x_2 = 20.3$ were used for the PEI-LCP blends and values of $x_1m = 60.5$ and $x_2 = 48.6$ were used for the PEEK-LCP blends. For the PEEK-LCP blends, the χ_{12} values have been found to be 0.069 ± 0.006 at 623 K. In Table 3, we can see that the χ_{12} of PEEK-LCP blends have almost same value whether the anisotropy of LCP is considered or not. This result may be because that the degree of disorder (y/x_1) of the LCP in the PEEK-LCP blends is very large which is approaching to almost a unit value. It is worth to note that the LCP becomes isotropic state when the y/x_1 has a unit value in the blend (1). In Table 3, the χ_{12} values of PEI-LCP blends have been calculated and found to be 0.181 ± 0.004 at 593 K when the anisotropy of the LCP is taken into account. When the anisotropy of the LCP is not considered, the χ_{12} values of PEI-LCP blends are shown to be 0.189 ± 0.008 at 593 K. For the PEI-LCP blend, the degree of disorder (y/x_1) is small compared with that of the PC-LCP and PEEK-LCP blends in Table 3.

Table 3. Polymer-polymer interaction parameter (χ_{12}) and degree of disorder (y/x_1) of blends of PEI-LCP and PEEK-LCP blends

Blends	Composition[a]	χ_{12}[b]	χ_{12}[c]	y/x_1[c]
PEI-LCP	0.9	0.197	0.185	0.67
	0.8	0.191	0.183	0.71
	0.7	0.182	0.176	0.76
PEEK-LCP	0.9	0.074	0.073	0.82
	0.8	0.066	0.065	0.89
	0.7	0.066	0.066	0.92

[a] Blend composition given as overall weight fraction of LCP in the each blends
[b] All values were calculated from eq. (5)
[c] All values were calculated from eqs. (2), (3), and (4)

Conclusions

In the study of the effect of blend composition on the T_{g1}(LCP) and T_{g2}(flexible chain polymer) of the blends of LCP with PEI and PEEK, a decrease of T_{g2} has been found for the PEI-LCP, and PEEK-LCP blends. For the PSF-LCP and PAS-LCP blends, the two T_gs do not changed with the blend compositions compared to their original T_gs. This result leads to the conclusion that PEI, and PEEK is partially miscible with the LCP but the PSF and PAS is immiscible with the LCP. From the results of the T_gs and ΔC_p of the PEI-LCP, and PEEK-LCP blends, it can be concluded that the LCP dissolves more in the PEI-, and PEEK-rich phase than does PEI and PEEK in the LCP-rich phase.

For the PEEK-LCP blends, the χ_{12} values have been calculated and found to be 0.069 ± 0.006 at 623 K. The χ_{12} of PEEK-LCP blends have almost same value whether the anisotropy of LCP is considered or not. This result may be because that the degree of disorder (y/x_1) of the LCP in the PEEK-LCP blends is very large which is approaching to almost a unit value. For the PEI-LCP blends, the χ_{12} values have been calculated and found to be 0.181 ± 0.004 at 593 K when the anisotropy of the LCP is taken into account. For the PEI-LCP blend, the degree of disorder (y/x_1) has small value compared with that of the PEEK-LCP blends when the anisotropy of LCP is considered.

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