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Thermal behavior and the determination of the polymer-polymer interaction parameter of polycarbonate and a thermotropic liquid crystalline polymer blends

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Summary

Thermal properties of the blends of polycarbonate (PC) and a thermotropic liquid crystalline polymer (LCP) prepared by screw extrusion have been investigated by differential scanning calorimeter (DSC). From the measured glass transition temperature (T_g) and specific heat increment (ΔC_p) at the T_g, the LCP appears to dissolve more in the PC-rich phase than does the PC in the LCP-rich phase. The polymer-polymer interaction parameter (χ_{12}) and the degree of disorder (y/x_1) of LCP in the PC-LCP blends were investigated using the lattice theory in which the anisotropy of LCP was taken into consideration. The χ_{12} of PC-LCP blend was calculated from the measured T_g and found to be 0.076 ± 0.008 at 250 °C. The y/x_1 of LCP in amorphous phase was found to be increased with the increase of PC weight fraction in the PC-LCP blends.

Introduction

In recent year, many researchers (1-7) have investigated the blend of polycarbonate (PC) and a thermotropic liquid crystalline polymer (LCP) in order to enhance the mechanical properties and the processibility of the blend. Because the miscibility of the flexible chain polymer and a liquid crystalline polymer could contribute to the physical properties of the blend, much of the recent attention has focused on the miscibility of the blend of flexible chain polymer such as PC and a liquid crystalline polymer (8-11).

There are two kinds of interaction between PC and LCP in the PC-LCP blends. One is chemical interaction such as transesterification and the other is physical interaction represented by such parameters as the Flory-Huggins interaction parameter (χ_{12}). The chemical interaction between PC and LCP has been investigated by Kosfeld and coworkers (8) using NMR. They reported that the transesterification occurred between PC and LCP in the PC-LCP blends when the blends were annealed over 270 °C. Nobil and coworkers (1) reported that the transesterification did not occur when the PC-LCP blends were annealed at 260 °C which temperature was a processing condition in melt extrusion. Friedrich and coworkers (9) have reported that PC is partially miscible with LCP using thermal analysis and the partial miscibility is ascribed to the physical mixing.

For the flexible-flexible polymer blend systems when the two polymers are partially miscible, the "T_g method" proposed by Kim and Burns (12-14) is available to determine the Flory-Huggins interaction parameter (χ_{12}). However, the Flory-Huggins theory may be

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inadequate to the system containing liquid crystalline polymer because the rod-like conformation of liquid crystalline polymer is excluded from the model (15, 16). For the blend system in which at least one component is LCP, the theoretical treatment of Flory and coworkers (17-19) in 1978 has opened an experimental field which can be covered with a great variety of materials and modifications available today.

In the present study, we examine thermal properties of screw-extruded blends of polycarbonate (PC) and a liquid crystalline polymer (LCP) consisting of poly(ethylene terephthalate) and p-hydroxy benzoic acid (PET/PHB). Also, we apply the Flory's lattice theory to the binary blend of flexible chain polymer and LCP in order to evaluate the χ_{12}-parameter. The entropy of mixing of the blend of flexible chain polymer and LCP was derived fully in this work and the empirical enthalpic term is used in the form of classical Flory-Huggins theory (15, 16). Using the lattice theory, we are examining the degree of disorder (y/x_1) and the polymer-polymer interaction parameter (χ_{12}) between PC and LCP.

Experimental

Polymers

The polymers used in this study were obtained from commercial sources. Polycarbonate (PC) designated as Trirex 3022 was supplied by Sam Yang Kasei Co., Ltd. Thermotropic liquid crystalline polymer designated as Rodrun 3000, manufactured by Unitika Co, was a random copolymer containing 60 mol % p-hydroxybenzoic acid (PHB) and 40 mol % poly(ethylene terephthalate) (PET). The characterization of the samples used in this study is summorized in Table 1.

Blends Preparations

To prepare melt blends, all polymers were dried in a vacuum oven at 120 °C for 24 hr before use. Blends were prepared using a 20 mm diameter laboratory scale screw extruder, with a 24:1 length-to-diameter screw. The length to diameter (L/D) ratio of the circular die was 20.0 with a diameter of 2 mm. The temperature of the extruder was set at 250 °C in the barrel zones and the die was kept at 240 °C.

Differential Scanning Calorimetry Measurements

The thermal properties of all samples were measured calorimetrically using a Perkin-Elmer differential scanning calorimeter, Model DSC-7.

Table 1.
Characterization of Polymer Samples Used in the PC-LCP Blends

	M_w	M_n	T_m (K)[a]	T_g (K)[a]	ΔC_p (J/gK)[a]	ρ (g/cm^3)[b]
PC	22,800[c]	9,760[c]	-	424.3	0.231	1.20
LCP	-	21,500[d]	474.1	331.5	0.052	1.40

[a] Measured in our laboratory using DSC.
[b] Measured in our laboratory using specific gravity chain balance.
[c] Data from supplier.
[d] Data from ref. 9.

Results and Discussion

T_gs of PC-LCP Blends

In Figure 1, we can see two glass transition temperatures (T_gs) of PC-LCP blends, which we designate as T_g(PC), associated with the PC-rich phase and T_g(LCP), associated with the LCP-rich phase. The T_g(PC) decreases about 24 K with the increase of LCP weight fraction by 0.9. The T_g(LCP) increases about 2 K with the increase of PC weight fraction by 0.5. Thus, the decrease in T_g(PC) is more pronounced than that of T_g(LCP). Here, the apparent PC weight fractions were determined in the PC-rich and LCP-rich phases by the following modified Fox equation (20) as reported by Kim and Burns (12)

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

where w_1' is the apparent weight fraction of polymer 1 in the polymer 1-rich phase, $T_{g1,b}$ is observed T_g of polymer 1 in the blends, and T_{g1} and T_{g2} are the T_gs of pure polymers 1 and 2, respectively.

ΔC_p of PC-LCP Blends

The values of specific heat increment (ΔC_P) at T_g for PC and LCP in the PC-LCP blends are presented in Figure 2. The ΔC_P of PC decreases with an increase in LCP weight fraction, whereas the ΔC_p of LCP decreases slightly with an increase in PC weight fraction.

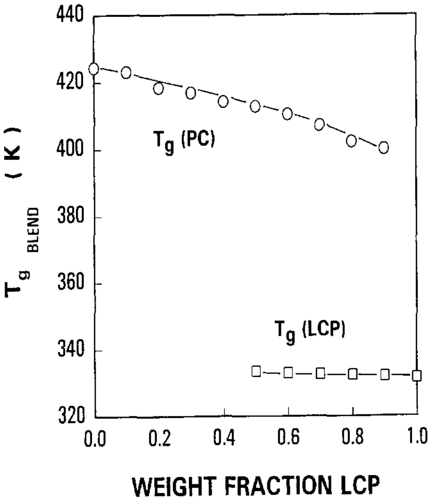

Fig. 1 Effect of blend composition on the T_g(PC) and the T_g(LCP) for PC-LCP blends.

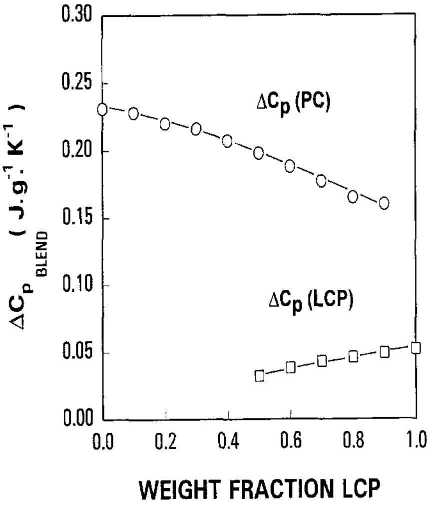

Fig. 2 Specific heat increment (ΔC_p) at the T_g(PC) and the T_g(LCP) for PC-LCP blends.

The reduction in the ΔC_p of one component results from the dissolution of that component in the conjugate phase (12-14). Thus, Figure 2 indicates that some of PC is dissolved in the LCP phase and some of LCP is dissolved in the PC phase. This result is consistent with the composition dependency of T_g shown in Figure 1.

Some researchers (1, 9) have reported that there occurs transesterification between PC and LCP when the blend is heated above 533 K. Because the PC-LCP blends used in the present work were prepared by melt extrusion at 523 K, the reductions in T_g(PC) and ΔC_p seen in Figures 1 and 2 should be ascribed to the physical mixing.

Applying eq. 1 to the DSC results measured for the blends, we have calculated the apparent weight fraction of LCP in the LCP-rich phase (w_1') and that of PC in the PC-rich phase (w_2''), which are presented in Table 2 and Figure 3. From Figure 3, we can see that the LCP dissolves more in the PC-rich phase (w_1'') than does the PC in the LCP-rich phase (w_2').

Transesterification between PC and LCP

The T_g(PC) and T_g(LCP) are shown in Figure 4, when the PC-LCP blends are annealed at 573 K for 30 min. The T_g(PC) of annealed PC-LCP blends decreases far significantly compared with the case of unannealed blends. Also we can see that the T_g(LCP) of annealed blends increases about 2 K compared with the case of unannealed blends. Similar result was reported by Friedrich and coworkers (9). They claimed that the depression of T_g(PC) was caused by transesterification occuring on annealing.

Polymer-Polymer Interaction Parameter (χ_{12}) of PC-LCP Blends

The thermotropic liquid crystalline polyester (LCP) can be treated as a freely-joined chain comprised of m rod-like segments of a same length as discussed in Flory's work (19).

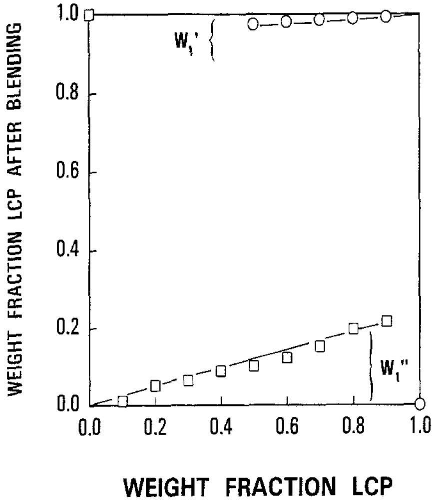

Fig. 3 Phase composition diagram of PC-LCP blends: weight fraction of LCP in PC-rich phase (□); weight fraction of LCP in LCP-rich phase (○).

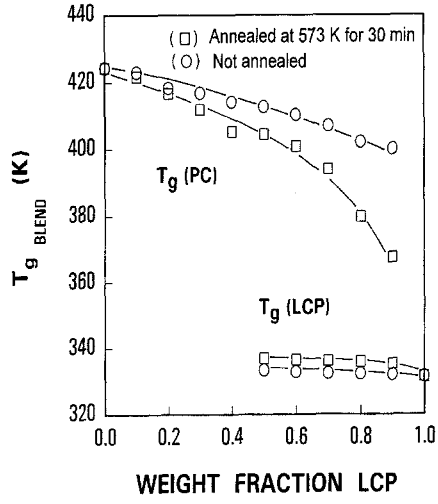

Fig. 4 Effect of annealing on the T_g(PC) and the T_g(LCP) for the PC-LCP blends.

Table 2.
The Apparent Volume Fraction, Degree of Disorder, and Polymer-Polymer Interaction Parameter of the PC-LCP Blends

Blend [a]	w_1' [b]	w_2'' [b]	v_1' [b]	v_2'' [b]	y/x_1 [c]	χ_{12} [d]	χ_{12} [e]
0.5	0.9740	0.8997	0.9762	0.9128	0.83	0.068	0.068
0.6	0.9808	0.8783	0.9825	0.8938	0.81	0.071	0.071
0.7	0.9863	0.8484	0.9875	0.8671	0.80	0.074	0.075
0.8	0.9890	0.8030	0.9900	0.8263	0.79	0.078	0.077
0.9	0.9931	0.7833	0.9937	0.8083	0.77	0.085	0.083

[a] Blend composition of LCP given as overall weight fraction in the PC-LCP blend.
[b] Single prime and double prime denote LCP-rich phase and PC-rich phase, respectively.
v_1' is calculated by using w_1' data, w_1' is calculated by eq. 1: $v_1'=1-v_2'$ and $v_2'=1-v_2''$.
[c] Degree of disorder of LCP in amorphous phase.
[d] All χ_{12}s are calculated by eqs. 8, 20 and 22: anisotropy of LCP is considered..
[e] All χ_{12}s are calculated by eq. 23: anisotropy of LCP is neglected.

A binary blend of flexible chain polymer and LCP can be treated as a fictitious ternary blend system composed by vacant cell (0), LCP (1), and flexible chain polymer (2), in which the fraction of a vacant cell is limited to zero. Then we apply the lattice theory proposed by Flory and coworkers to the blend of a flexible polymer and a LCP.
In this work, the configurational partition function is obtained as follow:

$$Z_M = \left[\frac{[n_T - n_1(mx_1 - my)]!}{(n_T - x_1 mn_1)! n_1! n_T{}^{n_1(my-1)}} \right] \times \left[\frac{(n_T - x_1 mn_1)! z_2{}^{n_2}}{(n_T - x_1 mn_1 - x_2 n_2)! n_2! n_T{}^{n_2(x_2-1)}} \right] \times \left[y^{2mn_1} \right] \qquad (2)$$

where $n_T=n_0+n_1mx_1+n_2x_2$ and m is the number of flexible joints in a LCP molecule. x_1 is the axis ratio of each of the m rods comprising the molecule, x_2 is the contour length of flexible chain polymer (the molar volume of repeating unit of flexible chain polymer is regarded as 1), y denotes disorientation (17) ($y=x_1\sin\phi$), and z_2 is the internal configuration partition function for the flexible chain polymer (18). The first and the second bracket in eq. 2 is combinatory part of liquid crystalline polymer and flexible chain polymer, respectively. The last bracket is the orientational part. The orientational part can be given more exactly by Flory-Ronca theory (21, 22). However, we adopt approximation value of orientational part in configurational partition function for the simplicity (21), which will be discussed in this work. The limit of complete disorder is $y=x_1$ in this work. When the liquid crystalline polymer has complete ordered structure, the orientation factor (y) has a unit value. When the fraction of a vacant cell is limited to zero, the eq. 2 reduces to eq. 3.

$$Z_M = \frac{[n_2 x_2 + ymn_1]! \, y^{2mn_1} z_2{}^{n_2}}{n_1! n_2! (n_1 mx_1 + n_2 x_2)^{n_1(my-1)+n_2(x_2-1)}} \qquad (3)$$

Introducing Stirling's approximation, one can obtain the following expressions

$$-\ln Z_M = n_1 \ln\left(\frac{v_1}{x_1 m}\right) + n_2 \ln\left(\frac{v_2}{x_2}\right) - (m_2 n_2 + myn_1) \ln\left[\frac{(m_2 n_2 + myn_1)}{(x_1 mn_1 + x_2 n_2)}\right])$$

$$+n_2(x_2 - 1 - \ln z_2) - n_1(m \ln y^2 - my + 1) \qquad (4)$$

or

$$-\ln Z_M = n_1 \ln(\frac{v_1}{x_1 m}) + n_2 \ln(\frac{v_2}{x_2}) - n_T[1 - v_1(1 - \frac{y}{x_1})]\ln[1 - v_1(1 - \frac{y}{x_1})]$$
$$+ n_2(x_2 - 1 - \ln z_2) - n_1(m \ \ln y^2 - my + 1) \qquad (5)$$

The partial molar entropy of mixing of anisotropic phase can be obtained as the partial derivative of eq. 5 with respect to n_1

$$\frac{\overline{\Delta s_1}}{R} = \ln(\frac{v_1}{x_1 m}) + v_1 x_1 m(\frac{y}{x_1} - \frac{1}{x_1 m}) + v_2 x_1 m(1 - \frac{1}{x_2}) + 2m(1 - \ln y) \qquad (6)$$

Similarly, the partial molar entropy of mixing of flexible chained polymer can be derived as

$$\frac{\overline{\Delta s_2}}{R} = \ln(\frac{v_2}{x_2}) + v_1 x_2(\frac{y}{x_1} - \frac{1}{x_1 m}) + v_2(x_2 - 1) - x_2 \ln[1 - v_1(1 - \frac{y}{x_1})] - \ln z_2 \qquad (7)$$

Equating $\frac{\partial \ln Z_M}{\partial y}$ to zero, the following expression can be obtained (17)

$$\exp(\frac{-2}{y}) = 1 - v_1(1 - \frac{y}{x_1}) \qquad (8)$$

After substitution of eq. 8 to the eq. 7 gives

$$\frac{\overline{\Delta s_2}}{R} = \ln(\frac{v_2}{x_2}) + v_1 x_2(\frac{y}{x_1} - \frac{1}{x_1 m}) + v_2(x_2 - 1) + \frac{2x_2}{y.} - \ln z_2 \qquad (9)$$

The partial molar entropy of mixing for isotropic phase can be obtained from the eqs. 6 and 9 when the disorientation factor (or disorder index: y) is the same as the axis ratio (x_1).

$$\frac{\overline{\Delta s_1}}{R} = \ln(\frac{v_1}{x_1 m}) + v_1(x_1 m - 1) + v_2 x_1 m(1 - \frac{1}{x_2}) - 2m \ \ln x_1 \qquad (10)$$

$$\frac{\overline{\Delta s_2}}{R} = \ln(\frac{v_2}{x_2}) + v_1 x_2(1 - \frac{1}{x_1 m}) + v_2(x_2 - 1) - \ln z_2 \qquad (11)$$

The enthalpy of mixing can be given by (15, 16)

$$\Delta H = \chi_{12} v_1 v_2 (x_1 m n_1 + x_2 n_2) RT \qquad (12)$$

where χ_{12} is the polymer-polymer interaction parameter between the flexible chain polymer and liquid crystalline polymer. v_1 and v_2 are the volume fraction of component 1 and 2, respectively. n_1 and n_2 are the number of moles of component 1 and 2, respectively. The partial molar enthalpy of mixing can be obtained as the partial derivative of eq. 12.

$$\Delta\overline{H_1} = x_1 m \chi_{12} v_2^2 RT \qquad (13)$$

$$\Delta\overline{H_2} = x_2 \chi_{12} v_1^2 RT \qquad (14)$$

Then the chemical potential of anisotropic phase can be obtained by combining eqs. 6, 9, and 13 such that

$$\frac{(\mu_1-\mu_1^o)}{RT}=\ln(\frac{v_1}{x_1m})+v_1x_1m(\frac{y}{x_1}-\frac{1}{x_1m})+v_2x_1m(1-\frac{1}{x_2})+2m(1-\ln y)+x_1m\chi_{12}v_2^2 \tag{15}$$

$$\frac{(\mu_2-\mu_2^o)}{RT}=\ln(\frac{v_2}{x_2})+v_1x_2(\frac{y}{x_1}-\frac{1}{x_1m})+v_2(x_2-1)+\frac{2x_2}{y}-\ln z_2+x_2\chi_{12}v_1^2 \tag{16}$$

Similarly, the chemical potential of isotropic phase can be obtained by combining eqs. 10, 11, and 14 such that

$$\frac{(\mu_1-\mu_1^o)}{RT}=\ln(\frac{v_1}{x_1m})+v_1(x_1m-1)+v_2x_1m(1-\frac{1}{x_2})-2m\ln x_1+x_1m\chi_{12}v_2^2 \tag{17}$$

$$\frac{(\mu_2-\mu_2^o)}{RT}=\ln(\frac{v_2}{x_2})+v_1x_2(1-\frac{1}{x_1m})+v_2(x_2-1)-\ln z_2+x_2\chi_{12}v_1^2 \tag{18}$$

At equilibrium the chemical potential of each component must be the same in both phases. Denoting anisotropic phase by single and isotropic phase by double primes, we have following expression for the liquid crystalline polymer.

$$\Delta\mu_1' = \Delta\mu_1'' \tag{19}$$

Then, we obtain the following expressions

$$\begin{aligned}&\ln(\frac{v_1'}{v_1''})+v_1'x_1m(\frac{y}{x_1}-\frac{1}{x_1m})-v_1''(x_1m-1)\\&+x_1m(1-\frac{1}{x_2})(v_2'-v_2'')+2m[1+\ln(\frac{x_1}{y})]+x_1m\chi_{12}(v_2'^{\,2}-v_2''^{\,2})=0\end{aligned} \tag{20}$$

Similarly, we have following expression for the flexible chain polymer

$$\Delta\mu_2' = \Delta\mu_2'' \tag{21}$$

$$\begin{aligned}&\ln(\frac{v_2'}{v_2''})+v_1'x_2(\frac{y}{x_1}-\frac{1}{x_1m})-v_1''x_2(1-\frac{1}{x_1m})\\&+(x_2-1)(v_2'-v_2'')+\frac{2x_2}{y}+x_2\chi_{12}(v_1'^{\,2}-v_1''^{\,2})=0\end{aligned} \tag{22}$$

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. 23 as reported by Kim and Burns (12-14).

$$\chi_{12}=\frac{\begin{aligned}&\{(\phi_1'^2-\phi_1''^2)[m_2\ln(\phi_1''/\phi_1')+(m_1-m_2)(\phi_2'-\phi_2'')\\&+(\phi_2'^2-\phi_2''^2)[m_1\ln(\phi_2''/\phi_2')+(m_2-m_1)(\phi_1'-\phi_1'')]\}\end{aligned}}{2m_1m_2(\phi_1'^2-\phi_1''^2)(\phi_2'^2-\phi_2''^2)} \tag{23}$$

where ϕ_1' is the apparent volume fraction of PC dissolved in the PC-rich phase, ϕ_1'' is the apparent volume fraction of PC dissolved in the LCP-rich phase. m_1 and m_2 are the number of lattice site of LCP and PC, respectively.

If the volume fractions in each phase are determined experimentally, then the polymer-polymer interaction parameter (χ_{12}) and degree of disorder (y/x_1) can be calculated by eqs. 8, 20 and 22 in equilibrium condition. The contour length of PC (x_2) and the total length of LCP (x_1m) were determined from the number average molecular weight (12). Values of $x_1m = 72.6$ and $x_2 = 38.4$ were used for LCP and PC, respectively.

In Table 2, the apparent volume fraction (v′), the polymer-polymer interaction parameter (χ_{12}), and the degree of disorder (y/x_1) are presented. The apparent volume fraction was obtained from the apparent weight fraction divided by densities of each polymer and the apparent weight fraction was determined by eq. 1 from measured glass transition temperatures.

In Table 2, the polymer-polymer interaction parameter (χ_{12}) of PC-LCP blend was calculated from the measured volume fraction and found to be 0.076 ± 0.008 at 523 K when the anisotropy of LCP in the PC-LCP blend was considered. When the anisotropy of LCP was not considered, the χ_{12} of PC-LCP blend was calculated by eq. 23 and found to be 0.077 ± 0.009 at 523 K. In Table 2, we can see that the χ_{12} has almost the same value when the anisotropy of LCP is considered or not. This result may be because that the degree of disorder (y/x_1) of LCP in the blend is very large which is approaching to almost a unit value (0.8±0.03). It is worth to note that the LCP becomes isotropic state when the y/x_1 has a unit value in the blend.

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