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Thermodynamic Analysis of the UCST-Type Phase Behavior of Polycarbonate Blends with Poly(ethylene-co-1,4-dimethyl cyclohexane terephthalate) Co-polyesters

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To understand upper critical solution temperature-type (UCST-type) phase behavior of polycarbonate (PC) blends with poly(ethylene-co-1,4-dimethyl cyclohexane terephthalate) (PECT) co-polyesters, thermodynamic analysis for the miscibility of these blends was performed with an equation-of-state theory. The bare interaction energy for each PC/PECT pair calculated from the phase homogenization temperatures of PC/PECT blends using the lattice-fluid theory was positive and increased with the 1,4-dimethyl cyclohexane (CHDM) content in PECT, whereas the phase homogenization temperature of PC/PECT blends observed in the previous study seemed to decrease with CHDM content. It was revealed that the observed decrease in blend phase homogenization temperature with CHDM content in PECT originated from equation-of-state effects, rather than from energetic effects.

Introduction

In the previous study,¹ we examined bisphenol A polycarbonate (PC) blends with poly(ethylene-co-1,4-dimethyl cyclohexane terephthalate) (PECT) that contained various amounts of 1,4-dimethyl cyclohexane (CHDM), to combine the beneficial properties of each polymer into a single product. PC/PECT blends were not miscible near room temperature, regardless of the PECT composition. However, PC blends with PECT that contained 32–80 mol % CHDM became miscible when heated, because of upper critical solution temperature-type (UCST-type) phase behavior. Based on this factor, the homogeneous PC/PECT blends that exhibit a single glass-transition temperature and have optical-grade clarity were successfully produced by quenching from the aforementioned phase homogenization temperature.¹

It is known that PC does not form miscible blends with poly(ethylene-terephthalate) (PET), whereas its blends with poly(1,4-dimethyl cyclohexane terephthalate) (PCT), which are prepared by melt mixing at ~300 °C, are miscible.^{2–4} Although the phase behavior of PC/PET, PC/PCT, and PC/PECT blends had been explored previously,^{1–4} the quantitative thermodynamic information involved in these blends was not characterized to date. Quantitative information about polymer–polymer interactions is an important element for controlling the phase behavior of blends, because the thermodynamic phase behavior of blends is dominated by these interactions. In this study, to understand the observed phase behavior of PC/PECT blends, the bare interaction energy involved in a blend was quantified from the observed phase boundaries, using an equation-of-state theory (i.e., lattice-fluid theory^{5–8}) combined with a binary interaction model.^{9,10} The terms related to the compressibility

and the combinatorial entropy of the PC/PECT blend were also quantified, and then the phase behavior of PC/PECT blend observed previously was explored with the thermodynamic information obtained here.

Materials and Procedure

Polymers used in the experiments and their pertinent information are listed in Table 1. Some are commercially available, whereas others are experimental materials. PECT co-polyesters were specially synthesized by SK Chemicals in Korea for the current work. According to the supplier, the co-polyesters consist of diol (ethylene glycol (EG) and CHDM) and terephthalic acid in a molar ratio of 1:1. The CHDM content of the co-polyester was determined using element analysis. The numerical part of the code for the co-polyester indicates the molar percentage of CHDM in the diol.

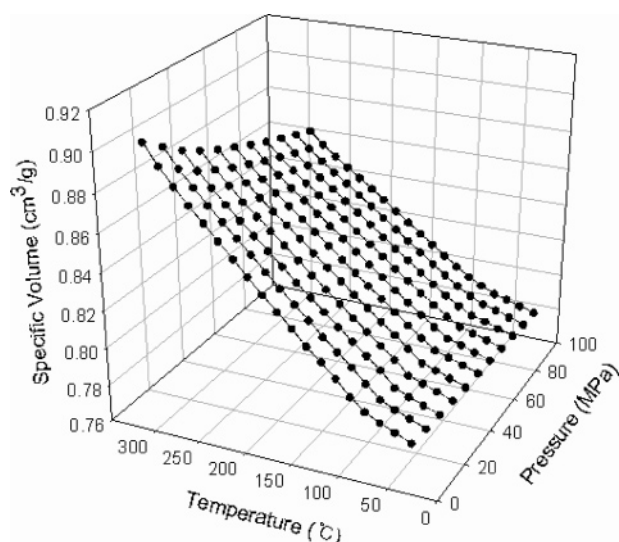
To evaluate the interaction energies responsible for the equilibrium phase behavior using an equation-of-state theory, pressure–volume–temperature (PVT) data for each component are required so that the characteristic parameters ($\tilde{P} = P/P^*$, $\tilde{T} = T/T^*$, and $\tilde{\rho} = 1/\tilde{V} = \rho/\rho^* = v^*/v$, where the asterisks denote characteristic parameters and \tilde{P} , \tilde{T} , and $\tilde{\rho}$ are reduced properties of pressure, temperature, and density, respectively) can be determined. The characteristic parameters of the PC that have been obtained from PVT data are known.¹¹ To obtain the characteristic parameters of PECT co-polyesters, the changes in the specific volume of PECT, as a function of temperature and pressure, were measured using a density gradient column and a Genimix PVT apparatus. Starting at 30 °C, a sample was compressed along 19 isotherms, spaced ~15 °C apart, up to 295 °C, with volume data recorded at pressure intervals of 10 MPa between 10 MPa and 200 MPa along each isotherm. The specific volume at zero pressure for each isotherm was obtained by extrapolation, using the Tait equation.¹²

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Table 1. Polymers Used in This Study

abbreviation ^a	Molecular Weight ^b		T_g (°C)	source
	weight-based, M_w	number-based, M_n		
PC	39 000	23 000	148	LG Chemicals (grade 300-10)
PECT 32	40 000	27 000	79	SK Chemicals (grade JN-100)
PECT 60	37 000	25 000	85	SK Chemicals
PECT 80	42 500	28 000	89	SK Chemicals

^a The numerical value included as part of the code for these co-polyesters indicates the nominal percent per mole of CHDM in diol. ^b Molecular weight information was provided by the suppliers.

**Figure 1.** Pressure–volume–temperature (*PVT*) behavior of PECT 32.**Table 2. Characteristic Properties of Polymers**

polymer	Characteristic Property		
	temperature, T^* (K)	pressure, P^* (bar)	density, ρ^* (g/cm³)
PC	802	4930	1.276
PECT 32	824	6118	1.2995
PECT 60	821	6037	1.2819
PECT 80	791	5953	1.2713

Results and Discussion

There are several equation-of-state theories accounting for the compressible nature of polymer mixtures. The phase behavior of the polymer mixtures (i.e., LCST or UCST) can be predicted with these theories. However, the following discussion is limited to the lattice-fluid theory, because this theory has a simpler and more-closed mathematical form and gives better results, in regard to predicting the phase behavior of polymer mixtures, than other methods.^{8,12,13}

Figure 1 shows selected *PVT* data of PECT 32 co-polyester obtained from isothermal experiments at pressures of 0–100 MPa and temperatures of 30–295 °C. The characteristic parameters of the lattice-fluid theory were obtained using a nonlinear least-squares method to fit the *PVT* data to the equation of state.^{5–8} The lattice-fluid theory shows systematic deviations in the regression at high pressure.^{8,13} Thus, only low-pressure data (0–100 MPa) data, where this is not a problem, were used for the calculations. To some extent, the characteristic parameters obtained are dependent on temperature; thus, to obtain the most-reliable results, the temperature range should include the range where the phase homogenization of PC/PECT blends occurs.^{13–15} Table 2 lists the characteristic parameters

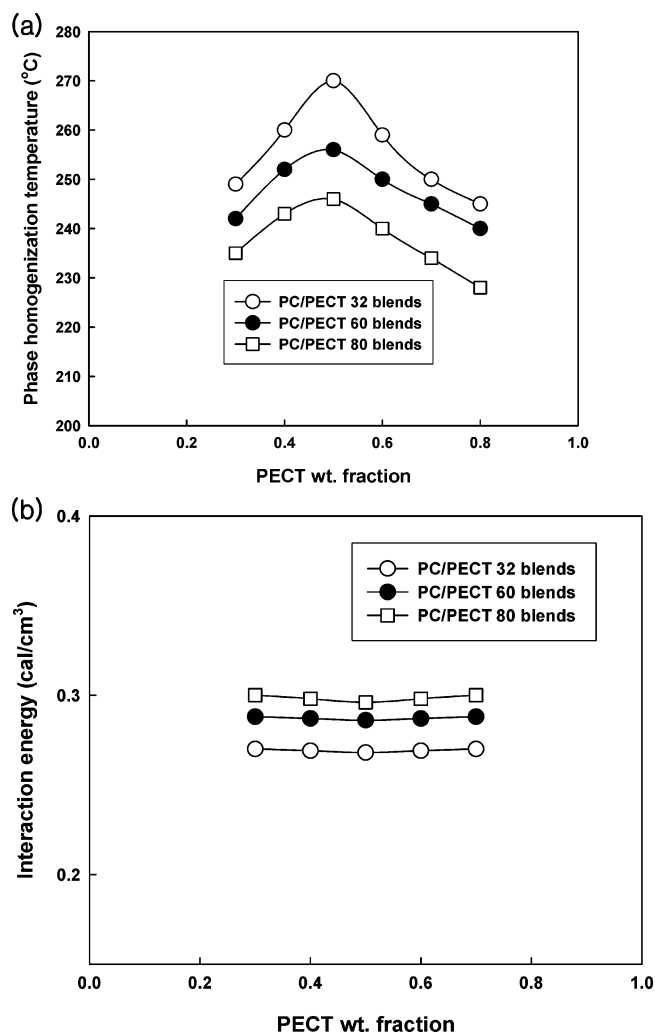


Figure 2. (a) UCST-type phase boundaries of PC blends with PECT co-polyesters containing various amounts of CHDM. Reproduced with permission from ref 1. (Copyright American Chemical Society, 2006.) (b) Interaction energies of the corresponding PC blends with PECT co-polyesters.

for PECT co-polyesters obtained from pressures of 0–100 MPa and temperatures of 205–295 °C.

As described in the previous study,¹ PC forms homogeneous mixtures with PECT co-polyesters that contain 32–80 mol % CHDM when heated, because of UCST-type phase behavior. The phase homogenization temperature of the blend was decreased as the CHDM content in PECT co-polyesters was increased, as shown in Figure 2a. (Note that Figure 2a is a reproduction of Figure 5 from ref 1.) This result indicates that the miscibility of the PC blend with PECT co-polymer is enhanced by increasing the CHDM content in PECT. To understand the observed phase behavior of the PC/PECT blends, the bare interaction energies of the PC/PECT blends were calculated from phase boundaries, using the lattice-fluid theory combined with the binary interaction model. The background details for the lattice-fluid model and the binary interaction model have been described previously.^{5–10,14,15} To extract information about the bare interaction energy from the phase boundaries, it is assumed that, to a good approximation, these data correspond to the spinodal curve.^{11,14,15}

In the lattice-fluid theory, the characteristic pressure of a mixture (P^*) is related to that of each component and the bare interaction energy (ΔP_{ij}^*) by^{8,12}

$$P^* = \sum_i \phi_i P_i^* - \sum_{i < j} \sum \phi_i \phi_j \Delta P_{(ij)}^* \quad (1)$$

For a binary blend of a random co-polymer composed of units 1 and 2 and a homopolymer composed of unit 3, the interaction energy between the co-polymer and the homopolymer ($\Delta P_{(ij)}^*$) is given, in terms of monomer unit pair interactions,^{9,10} by

$$\Delta P_{(ij)}^* = \Delta P_{13}^* \phi'_1 + \Delta P_{23}^* \phi'_2 - \Delta P_{12}^* \phi'_1 \phi'_2 \quad (2)$$

where ϕ'_i indicates the close-packed volume fraction of component i in the co-polymer. The free energy of mixing per unit volume, g , is given by

$$g = RT \sum_i \frac{\phi_i}{v_i^*} \ln(\phi_i) \pm \tilde{\rho} P^* + P\tilde{v} + \frac{RT}{v^*} \left(\frac{1 - \tilde{\rho}}{\tilde{\rho}} \ln(1 - \tilde{\rho}) + \frac{\ln(\tilde{\rho})}{r} \right) \quad (3)$$

where the first term is the combinatorial entropy and the remaining two terms represent the noncombinatorial free energy. The spinodal condition for a compressible mixture can be written as

$$\frac{d^2 g}{d\phi^2} = g_{\phi\phi} - \frac{(g_\phi)^2}{g_{\tilde{\rho}}} = 0 \quad (4)$$

where $d^2 g/d\phi^2$ is the second derivative of the free energy of mixing per unit volume, with respect to ϕ , and the subscripts ϕ and $\tilde{\rho}$ indicate partial derivatives, with respect to ϕ or $\tilde{\rho}$. In terms of the lattice-fluid theory, the indicated derivatives for binary mixture are given by^{8,14}

$$g_{\phi\phi} = -2\tilde{\rho}\Delta P^* + RT \left(\frac{1}{\phi_1 r_1 v_1^*} + \frac{1}{\phi_2 r_2 v_2^*} \right) \quad (5)$$

$$g_{\tilde{\rho}\phi} = -[P_1^* - P_2^* - (1 - 2\phi_1)\Delta P^*] + \frac{RT}{\tilde{\rho}} \left(\frac{1}{r_1 v_1^*} - \frac{1}{r_2 v_2^*} \right) - RT \left(\frac{1}{v_1^*} - \frac{1}{v_2^*} \right) \left[\frac{\ln(1 - \tilde{\rho})}{\tilde{\rho}^2} + \frac{1}{\tilde{\rho}} \right] \quad (6)$$

$$g_{\tilde{\rho}} = \frac{RT}{v^*} \left[\frac{2 \ln(1 - \tilde{\rho})}{\tilde{\rho}^3} + \frac{1}{\tilde{\rho}^2(1 - \tilde{\rho})} + \frac{1}{\tilde{\rho}^2} \left(1 - \frac{1}{r} \right) \right] \quad (7)$$

The ΔP^* values for blends of PC with PECT co-polyesters ($\Delta P_{\text{PC-PECT}}^*$) were calculated from the phase boundaries shown in Figure 2a, using eq 4. Figure 2b shows that the $\Delta P_{\text{PC-PECT}}^*$ values obtained for PC/PECT 32 blends ($\Delta P_{\text{PC-PECT 32}}^*$) are essentially independent of composition, as described in the lattice-fluid theory.⁵⁻⁸ The bare interaction energies of PC blends with other PECT co-polyesters exhibit similar trends with those of PC/PECT 32 blends.

The observed phase homogenization temperature of PC/PECT blends indicates that the miscibility of PC with PECT co-polyesters seem to have been enhanced as the CHDM content in the co-polyesters increased. However, the bare interaction energy for the PC/PECT pair was positive and gradually increased as the CHDM content in the PECT co-polyesters increased, as shown in Figure 2b. It is generally expected that blends with more-favorable energetic interaction (a lower ΔP^* value) have lower UCST (or higher LCST). This means that the observed phase behavior of PC/PECT blends cannot be explained by the obtained $\Delta P_{\text{PC-PECT}}^*$ value, which reflects

only energetic issues and is free of residual entropy effects (equation-of-state effects). For detailed analysis of the observed behavior of PC/PECT blends, the phase stability condition of the lattice-fluid theory (eq 4) was analyzed as described in the following discussion.

For the phase stability, the gradient term in eq 4 (i.e., $d^2 g/d\phi^2$) should be positive. The indicated derivatives in eq 4 are approximately given by¹⁵

$$\frac{d^2 g}{d\phi^2} \approx -2\tilde{\rho}\Delta P^* + RT \left(\frac{1}{\phi_1 r_1 v_1^*} + \frac{1}{\phi_2 r_2 v_2^*} \right) - \left(\frac{R}{v^*} \right)^2 (T_1^* - T_2^*)^2 \kappa \tilde{\rho}^3 > 0 \quad (8)$$

where ΔP^* is the bare interaction energy between PC and PECT; T_1^* and T_2^* are the characteristic temperature of PC and PECT, respectively; and κ is the isothermal compressibility of the binary mixture. The explanation for the observed phase behavior of blends is revealed by the three terms in eq 8, which comprise the stability condition. The bare interaction energy (the first term in eq 8) between PC and PECT becomes less favorable for miscibility of the blend with increasing CHDM content in PECT. Because the molecular weights of PECT co-polyesters are almost the same, as listed in Table 1, the combinatorial entropy terms (the second term in eq 8), which is favorable for miscibility and increases with temperature, are similar, regardless of the types of PECT used here. The characteristic temperature for the PECT co-polyester (T_2^*) becomes smaller as the CHDM content increases. It is known that T^* is related to the solubility parameter and the solubility parameter of PECT becomes smaller as the CHDM content increases.^{12,16} Therefore, the T^* values for PECT (or the solubility parameters for PECT) are ranked in the following order:

$$\text{PECT 32} > \text{PECT 60} > \text{PECT 80}$$

As a result, the difference in the characteristic temperature, $|T_1^* - T_2^*|$, becomes smaller as the CHDM content increases (see Table 2). This means that the contribution of this term to the phase stability becomes more favorable as the CHDM content increases. The reduced density becomes smaller as the CHDM content increases. At a given temperature, a smaller reduced density results in a larger isothermal compressibility of the co-polyester. The increased compressibility caused by the incorporation of CHDM deters phase homogenization. As a consequence, the energetic interaction and compressibility become less favorable for phase stability as the CHDM content increases, while the difference in the characteristic temperature becomes more favorable. This observation means that the phase separation temperature is determined by the competition among these terms in eq 8. To show this relationship more clearly, the $d^2 g/d\phi^2$ term was plotted as a function of temperature. Figure 3 shows the calculated $d^2 g/d\phi^2$ values of PC/PECT 32 (50/50 pair), PC/PECT 60 (50/50 pair), and PC/PECT 80 (50/50 pair), as a function of temperature. It was revealed that the observed decrease in the phase homogenization temperature of the blend, caused by the increasing CHDM content in the PECT co-polyester, stems from equation-of-state effects (mainly, a reduction in $|T_1^* - T_2^*|$, rather than from energetic effects.

Summary

The bare interaction energies between polycarbonate (PC) and various poly(ethylene-co-1,4-dimethyl cyclohexane terephthalate (PECT) co-polyesters were calculated from the phase homogenization temperatures of these blends, using the lattice-

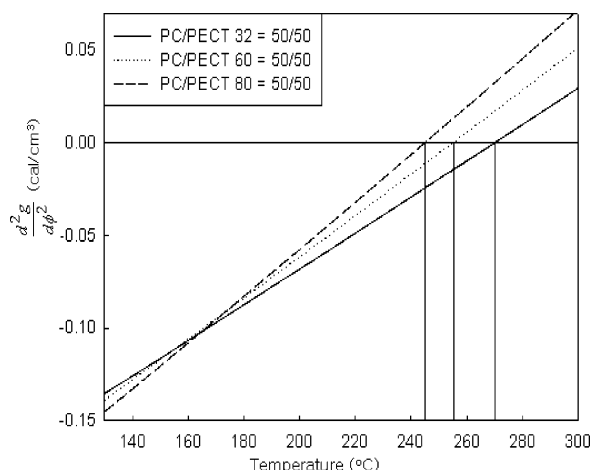


Figure 3. Change in the $d^2g/d\phi^2$ values of PC/PECT32, PC/PECT60, and PC/PECT80 blends (at 50/50 blend composition) with temperature.

fluid theory. The obtained bare interaction energy for a PC/PECT pair was positive and increased as the 1,4-dimethyl cyclohexane (CHDM) content in the PECT co-polyesters increased, whereas the miscibility of PC with PECT co-polyesters seemed to be enhanced as the CHDM content in the co-polyesters increased. To understand the observed behavior of the PC/PECT blends, the phase stability condition of the lattice-fluid theory was analyzed. The observed decrease in phase homogenization temperature of the blend, which seemed to be caused by the increasing CHDM content in the PECT co-polyester stems from equation-of-state effects (mainly, a reduction in $|T_1^* - T_2^*|$), rather than from energetic effects.

Acknowledgment

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