Miscibility of Branched Polycarbonate Blends with Poly(ethylene-co-1,4-dimethyl cyclohexane terephthalate) Copolyesters

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Abstract: The phase behavior of branched polycarbonate (BPC) blends with poly(ethylene terephthalate-co-1,4-dimethyl cyclohexane terephthalate) copolyesters (PECT), as well as their rheological properties, were assessed. Even though BPC blends with PECT prepared by solvent casting proved to be immiscible, BPC and PECT copolyesters containing 1,4-dimethyl cyclohexane (CHDM) from 32 to 80 mole% formed homogeneous mixtures upon heating. The homogenization temperatures of the blends decreased with increasing CHDM content in PECT. The interaction energies of the BPC-PECT pairs calculated from the phase boundary in accordance with the lattice-fluid theory were positive and also decreased with increasing CHDM content in PECT. It was shown that the phase homogenization of these blends occurs upon heating when the combinatorial entropy term, which is favorable for miscibility, overcomes unfavorable energetic terms at elevated temperatures. A novel product, which is not limited by the drawbacks of linear polycarbonate (PC) and evidences processability superior to that of the PC/PECT blends, can be developed via the blending of BPC and PECT.

Keywords: branched polycarbonate, poly(ethylene-co-1,4-dimethyl cyclohexane terephthalate) copolyesters, upper critical solution temperature, interaction energy, processability, transparency.

Introduction

Linear polycarbonate (PC) is widely used in automobile parts, electrical parts, optical parts, sheets, and media materials for audio and visual systems.[1] The main advantages of PC over other polymers are transparency with toughness, rigidity, high heat deflection temperature, dimensional stability, and self-extinguishing characteristics. However, PC has problems in the resistance to solvent stress cracking and UV stability. Furthermore, its poor processability caused by high melt viscosity deterred its application to the thin-section parts such as lenses for headlights and auxiliary lighting, cellular phone covers and lenses, and sports and safety eyewear glasses. To overcome drawbacks of PC still maintaining its optical transparency, numerous studies related to the PC blends have been performed. The focus of attention is directed to find homogeneous mixture and to explore the beneficial properties that may be gained by blending. PC blends with polyesters, both aliphatic and those containing aromaticity have been investigated extensively.[2-24] From early investigations related to the PC blends with polyester, it was confirmed that PC formed miscible blends with aliphatic polyesters containing approximately between two

and seven methylene segments per ester group[4-6] and with polyesters containing alicyclic structures.[16,18-20] Miscible PC blends with semi-aromatic polyesters such as poly(1,4-dimethyl cyclohexane terephthalate) (PCT) have been also reported in the literatures.[1-3,16,21] Among these miscible blends, PC blends with polyester containing alicyclic structure are using commercially as optical grades (GE, trade name: xylex[®]). Even though PC blends with aliphatic polyesters or with PCT are miscible, these blends are opaque because of the crystalline in polyesters.

Poly(ethylene-co-1,4-dimethyl cyclohexane terephthalate) (PECT) is a copolyester with optical clarity, chemical resistance, and excellent processability. However, low glass transition temperature of PECT deterred its application. Blending of PC with PECT offers attractive opportunity for the development of novel materials exhibiting useful combination of the properties. Compared to PC, the PECT in blend provides enhanced chemical resistance and permits lower processing temperatures than PC. Based on this, in previous study, we had examined PC blends with PECT containing various amounts of 1,4-dimethly cyclohexane (CHDM).[25] PC/PECT blends were not miscible at around room temperature regardless of PECT composition. However, PC blend with PECT containing CHDM from 32 to 80 mole% became miscible upon heating because of upper critical solution

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temperature type (UCST-type) phase behavior.

Polycarbonates are divided into linear polycarbonate (PC) and branched polycarbonate (BPC) according to its molecular structure. The rheological behavior of BPC differs from that of PC. The former exhibits pronounced structural viscosity.[1] When the shear rate is increased up to the non-Newtonian flow region, the decreasing rate of the melt viscosity of the former with shear rate is greater than that of the latter. This means that melt viscosity of PC/PECT blends may be further reduced by using BPC instead of PC at a shear rate region for the injection molding process. To develop miscible blends having better processability than PC/PECT blends and exhibiting optical-grade clarity, in this study, the miscibility of BPC blends with PECT copolyesters containing various amounts of CHDM unit and their processability were explored.

Experimental

The polymers used in this study were listed in Table I. BPC and PC supplied by LG-Dow Polycarbonate were commercial grades named as 302-7 and 300-10, respectively. PECT copolyesters were obtained from SK Chemicals. A PECT copolyester designated PECT60 was a commercial grade (trade name: JN-100), while other PECT copolyesters were experimental grades specially synthesized for this study. According to the supplier, copolyesters consist of diol (EG and CHDM) and terephthalic acid in a molar ratio of 1/1. The numerical value included as part of the code for these copolyesters indicates the nominal percent by mole of CHDM of the total diol composition in the copolyester. BPC and PECT were dried in a vacuum oven for a day prior to processing at 120 and 80 °C, respectively.

The blends of PC and PECT32 (or PECT60) were prepared in film form from casting solutions containing 5 wt% total polymers in methylene chloride. The casting solutions were dried at room temperature until most of the solvent had evaporated, and then the resulting films were further

Table I. Polymers Used in This Study

Abbreviation[a]	$\overline{M_W}$[b]	$\overline{M_n}$[b]	T_g (°C)	Source
PC	39,000	23,000	148	LGDow Polycarbonate (Grade 300-10)
BPC	43,000	26,000	147	LGDow Polycarbonate (Grade 302-7)
PECT5	38,000	26,000	93	SK Chemicals
PECT32	40,000	27,000	79	SK Chemicals
PECT60	37,000	25,000	85	SK Chemicals (Grade JN-100)
PECT80	42,500	28,000	89	SK Chemicals

[a]The numerical value included as part of the code for these copolyesters indicates the nominal percent by mole of CHDM of the total diol composition in the copolyester. [b]Molecular weight information was provided by suppliers.
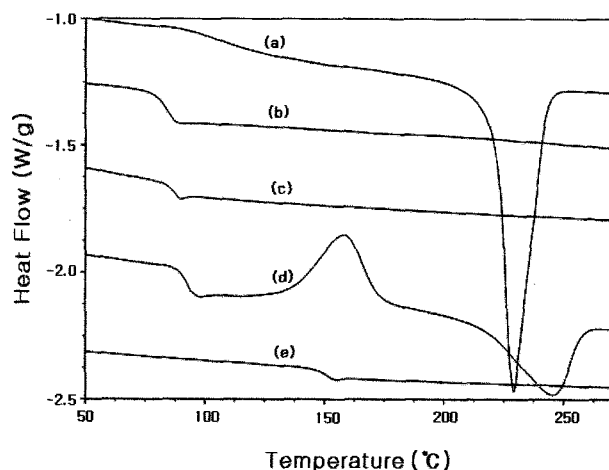
dried in a vacuum oven at 120 °C for a week. Since PECT5 and PECT80 copolyesters are not soluble in methylene chloride, the blends of BPC with these copolyesters were prepared via solution casting from o-chlorophenol. After drying in an air circulating oven at 120 °C for a day to remove most of the solvent, the blends were finally dried in a vacuum oven at 120 °C for a week. Blends were also prepared by melt mixing. Melt mixing was performed in a twin screw extruder (Bau Tech, model: BA-11, L/D ratio = 40). Melt mixed blends were immediately quenched into water bath after extrusion.

Transition temperatures of blends were measured at a heating rate of 20 °C/min by using DSC (TA Instrument, model: DSC-2010). The first scan was run to 300 °C to erase previous thermal history during sample preparation, and then the sample was quenched to room temperature to start the second scan. T_g was defined as the onset of change in the heat capacity. The phase homogenization temperature caused by the upper critical solution temperature (UCST) type phase behavior was measured by an annealing technique to access the closest true equilibrium temperature.[26-31] Changes in morphology of blends with temperature were also observed by an image analyzer [Bummi Universe, model: I-Top] equipped with a hot stage [Linkam THMS 600].

For the evaluation of the interaction energies responsible for the equilibrium phase behavior using an equation-of-state theory, pressure-volume-temperature (P-V-T) data for each component are required so that 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 PECT copolyesters obtained from P-V-T data were determined previously.[25] To obtain the characteristic parameters of BPC, the changes in the specific volume of BPC as a function of temperature and pressure were measured using a density gradient column and a Genomix PVT apparatus. The rheological measurements were carried out in a rheometer (Model: Physica MCR 500, Anton Parr, Germany, geometry: 25 mm parallel plate). The measurements were made at 280 °C in the shear rate range of 0.1 to 1000 sec⁻¹.

Results and Discussion

Phase Behavior of BPC/PECT Blends. PECT copolyesters as received samples were transparent except PECT5. Figure 1 shows DSC thermograms of BPC and various PECT copolyesters. For PECT5, a melting endotherm (229 °C) was observed upon heating. PECT32 and PECT60 showed a T_g at 79 and at 85 °C, respectively. For PECT80, a crystallization exotherm (158 °C) was observed upon heating above the T_g (89 °C) and then crystalline formed during heating was melted at 247 °C. Figure 2 shows DSC thermograms of

Figure 1. DSC thermograms of BPC and various PECT copolyesters; (a) PECT5, (b) PECT32, (c) PECT60, (d) PECT80, and (e) BPC.
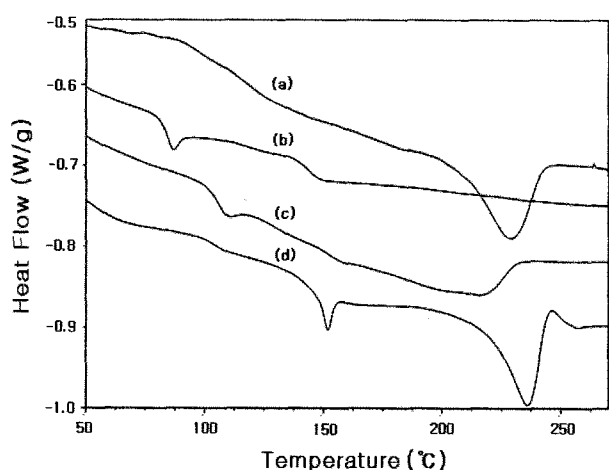

Figure 2. DSC thermograms of BPC/PECT = 50/50 blends (first scan) prepared by solvent casting. Note that the first scan was run from room temperature to 300 °C; (a) BPC/PECT 5 = 50/50, (b) BPC/PECT32 = 50/50, (c) BPC/PECT60 = 50/50, and (d) BPC/PECT80 = 50/50.

BPC/PECT = 50/50 blends prepared by solvent casting. The blends cast from solvent were translucent, and each DSC thermogram showed two T_gs indicating that phase separation occurred. Figure 3 exhibits thermograms of BPC/PECT = 50/50 blends observed at the second scan after the first scan was run to 300 °C. BPC blends with PECT copolyesters containing CHDM from 32 to 80 mole% exhibited a single T_g at a temperature intermediate between the glass transition of BPC and PECT. However, thermogram of BPC blend with PECT 5 still showed two T_gs. All blends prepared at other compositions showed a similar thermal behavior. These results indicated that BPC formed homogeneous mixtures with PECT copolyesters containing CHDM from 32 to
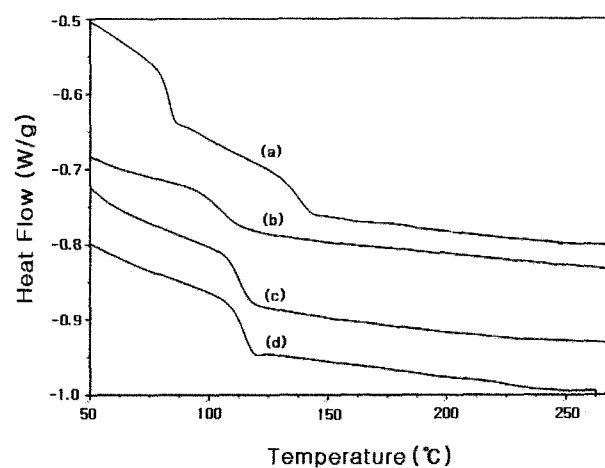

Figure 3. DSC thermograms of BPC/PECT = 50/50 blends observed at the second scan after the first scan was run to 300 °C; (a) BPC/PECT5 = 50/50, (b) BPC/PECT32 = 50/50, (c) BPC/PECT60 = 50/50, and (d) BPC/PECT80 = 50/50.
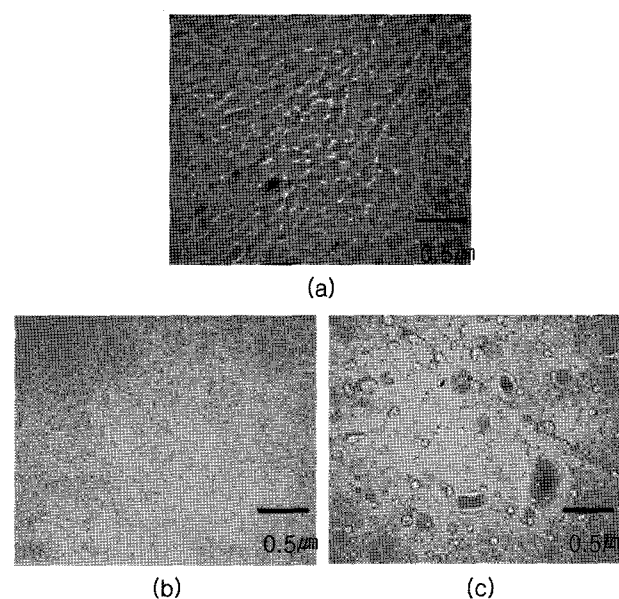

Figure 4. The morphology changes of BPC/PECT 60 = 60/40 blend with temperature. (a) morphology of blend prepared by solvent casting, (b) blend morphology observed at 265 °C. Note that blend was heated rapidly to a temperature about 200 °C and then heated at a rate of 5 °C/min, and (c) the obtained blend morphology when homogeneous blend at 265 °C was cooled to 255 °C at a rate of 5 °C/min.

80 mole% upon heating. Similar results were observed with PC/PECT blends.[25]

When the phase separated polymer mixture reaches the upper critical solution temperature (UCST) upon heating, it undergoes phase homogenization. Phase homogenization temperatures of blends caused by UCST-type phase behavior were measured by an annealing technique.[26-31] For exam-

ple, the BPC/PECT60 = 60/40 blend (Figure 4(a)) was heated rapidly to a temperature about 200 °C and then heated at a rate of 5 °C/min. As shown in Figure 4(b), blend became transparent and changes in the image were observed at 265 °C. Note that phase separation occurred again when homogeneous blend at 265 °C was cooled to 255 °C at a rate of 5 °C/min (Figure 4(c)). After determining the temperature at which phase homogenization occurred, blend specimens were annealed in the hot stage at a fixed temperature for 5 min. The blend annealed at 255 °C was still opaque and changes in the morphology of the blend were not observed while that annealed at 265 °C became clear and changes in the morphology were observed during annealing, i.e., domains existing in the matrix disappeared completely. The phase homogenization temperature of this blend would appear to lie between 255 and 265 °C. By successively repeating annealing process between 255 and 265 °C, the location of the UCST-type phase boundary was determined as shown in Figure 5.

As shown in Figure 5, the phase homogenization temperature curves for BPC/PECT blends are all very similar with each showing a maximum at about 50 wt% BPC. Note that phase homogenization did not occur upon heating until thermal degradation temperature (330 °C) when BPC blended with PECT 5. The phase homogenization temperature of blends increases in the order of BPC/PECT80 < BPC/PECT60 < BPC/PECT32. These results indicates that the blends that showed single T_g and optical clarity could be produced when blends exhibiting USCT-type phase behavior were taken above the homogenization temperature and quenched back to the room temperature. To explore this issue, BPC/PECT 60 = 50/50 blends prepared by melt mixing at 280 °C in a twin extruder were immediately quenched into water bath.
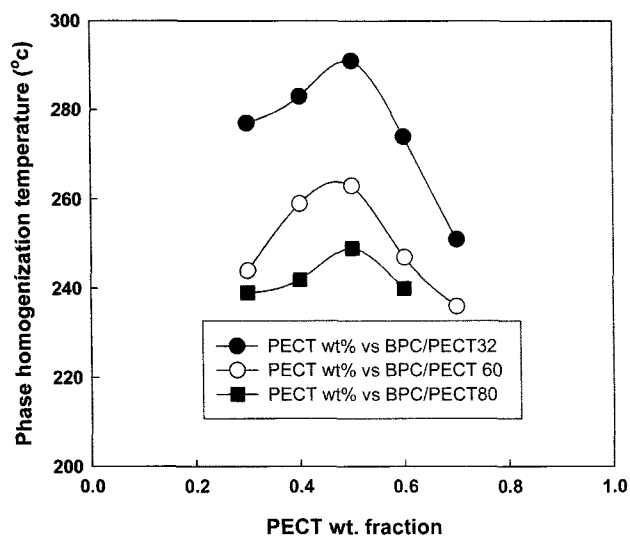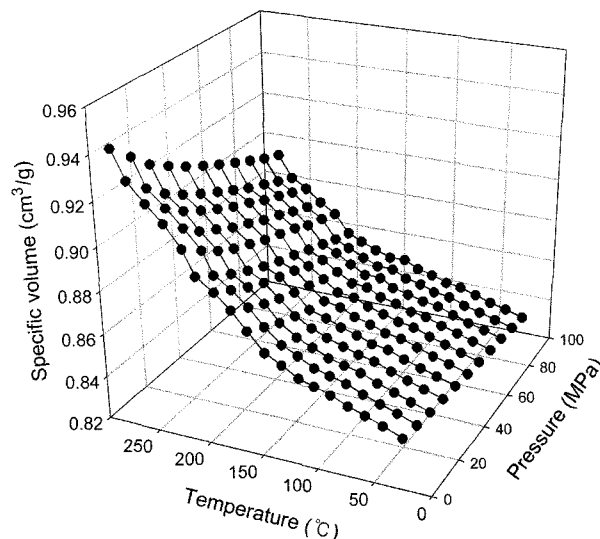

Figure 6. Pressure-volume-temperature behavior of BPC.

Melt mixed BPC/PECT60 = 50/50 blend were transparent and DSC thermogram of this blend exhibited a single T_g.

Interaction Energies of BPC/PECT Pairs. To understand the observed phase behavior of PC/PECT blends, the interaction energies of the PC/PECT blends were calculated from phase boundaries using the lattice-fluid theory. The detail background for the lattice-fluid model and binary interaction model were described previously.[27,32-36] The characteristic parameters of BPC were obtained from P-V-T data shown in Figure 6 by using a non-linear least squares method to fit the P-V-T data to the equation-of-state. The characteristic parameters of PECT copolyesters determined previously[25] and those of BPC were listed in Table II. In the lattice-fluid theory, the free energy of mixing, g, is given by

$$g = RT\sum_i \frac{\phi_i}{v_i^* r_i} \ln\phi_i + -\tilde{\rho}P^* + P\tilde{v}$$

$$+ \frac{RT}{v^*}\left(\frac{1-\tilde{\rho}}{\tilde{\rho}}\ln(1-\tilde{\rho}) + \frac{\ln\tilde{\rho}}{r}\right) \qquad (1)$$

where the first term is the combinatorial entropy and the remaining two terms are the non-combinatorial free energy. The phase stability condition for a compressible mixture can be written

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

Table II. Characteristic Properties of Polymers

Polymer	T^* (K)	P^* (bar)	ρ^* (g/cm³)
BPC	822	4966	1.2349
PECT 32	824	6118	1.2995
PECT 60	821	6037	1.2819
PECT 80	791	5953	1.2713

Figure 5. UCST-type phase boundaries of BPC blends with PECT copolyesters containing various amounts of CHDM.

where $d^2g/d\phi^2$ is the second derivative of the free energy of mixing with respect to ϕ and the subscripts ϕ and ρ indicate partial derivatives with respect to ϕ or ρ. In terms of the lattice-fluid theory, the indicated partial derivatives for binary mixture are given by[27,36]

$$g_{\phi\phi} = -2\rho\Delta P^* + RT\left(\frac{1}{\phi_1 r_1 v_1^*} + \frac{1}{\phi_2 r_2 v_2^*}\right) \quad (3)$$

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

$$- RT\left(\frac{1}{v_1^*} - \frac{1}{v_2^*}\right)\left(\frac{\ln(1-\rho)}{\rho^2} + \frac{1}{\rho}\right) \quad (4)$$

$$g_{\rho\rho} = \frac{RT}{v^*}\left(\frac{2\ln(1-\rho)}{\rho^3} + \frac{1}{\rho^2(1-\rho)} + \frac{1}{\rho^2}\left(1 - \frac{1}{r}\right)\right) \quad (5)$$

Where ΔP^* is interaction energy of BPC-PECT binary pair. The ΔP^* values ($\Delta P^*_{BPC-PECT}$) for blends of BPC with PECT copolyesters were calculated from phase homogenization temperatures shown in Figure 5 using eq. (2). The interaction energy for PC-PECT pair was positive and gradually decreased by increasing CHDM content in PECT copolyesters. Note that interaction energies of binary pairs were $\Delta P^*_{BPC-PECT32} = 0.35$ cal/cm^3, $\Delta P^*_{BPC-PECT60} = 0.30$ cal/cm^3, and $\Delta P^*_{BPC-PECT80} = 0.13$ cal/cm^3.

When interaction energy value is positive, UCST-type phase behavior of polymer-polymer pair is driven by combinatorial entropy term, which is favorable for miscibility and gradually increased with temperature. When this term is greater than unfavorable interaction energy term at an elevated temperature, miscible blend caused by UCST-type phase behavior is formed. To explore this more clearly, changes in $d^2g/d\phi^2$ of BPC-PECT pairs as a function of temperature was examined. Note that blend is miscible when
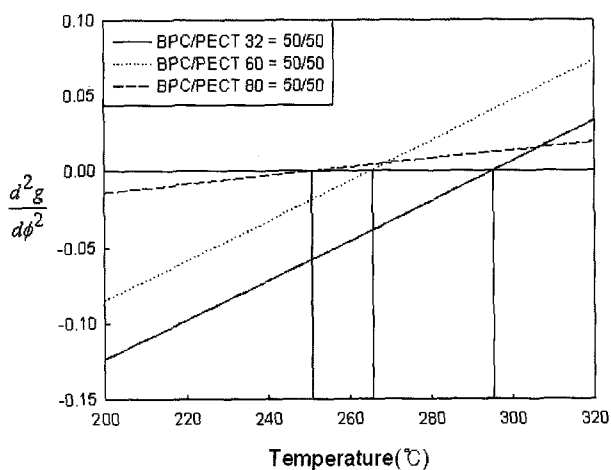
$d^2g/d\phi^2$ in eq. (2) is positive. As shown in Figure 7 for BPC/PECT32 = 50/50 blend, BPC/PECT60 = 50/50 blend, and BPC/PECT80 = 50/50 blend, $d^2g/d\phi^2$, which is negative at a low temperature range, is gradually increased with temperature and then becomes positive at phase homogenization temperature. It is generally expected that blends with more favorable energetic interaction (lower ΔP^* value) have lower UCST (or higher LCST). This means that the observed phase behavior of PC/PECT blends follows the same trends with other polymer-polymer blends.

Viscosity Changes with Shear Rate. Since BPC blends with various PECT60 copolyesters become homogeneous
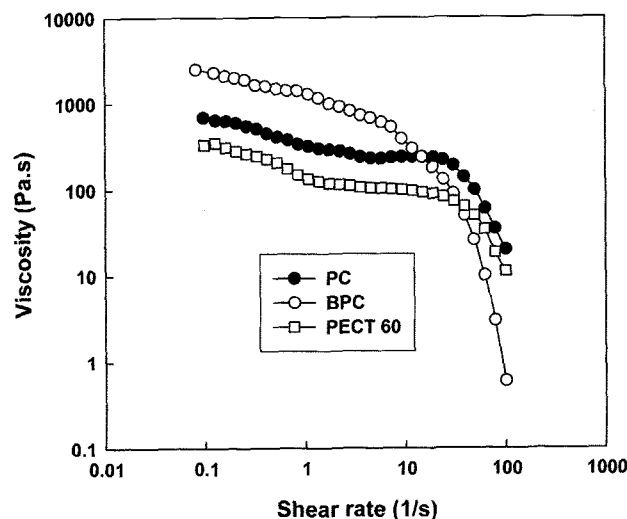

Figure 8. The measured viscosities of BPC, PC, and PECT32 as a function of shear rate at 270 °C.

Figure 7. Changes in the $d^2g/d\phi^2$ values of BPC/PECT32, BPC/PECT60 and BPC/PECT80 blends at 50/50 blend composition as a function of temperature.
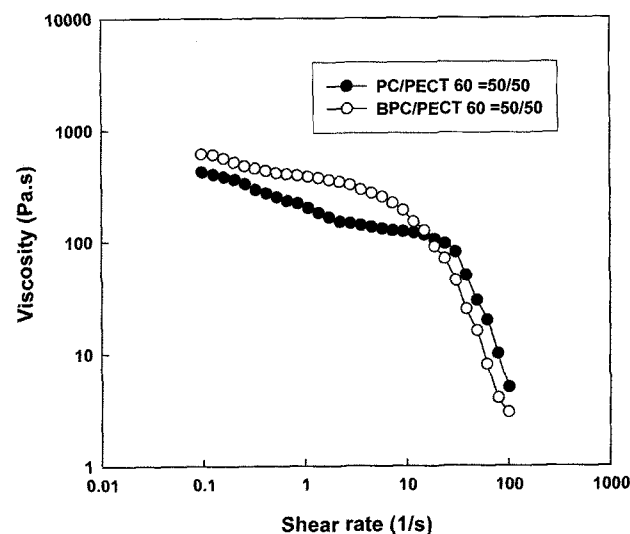

Figure 9. The measured viscosities of BPC/PECT60 = 50/50 blend and PC/PECT60 = 50/50 blend as a function of shear rate at 270 °C.

when temperature is higher than 270 °C, viscosities of homopolymers and their blends were measured at 270 °C. Figure 8 exhibits the measured viscosities of BPC, PC, and PECT60 as a function of shear rate. Viscosity of BPC is higher than that of PC at a low shear rate range. However, the viscosity decreasing rate of the former with shear rate is greater than that of the latter at a high shear rate region, and then viscosity of the former becomes lower than that of the latter. As shown in Figure 9, viscosity of BPC/PECT60 = 50/50 blend is lower than that of PC/PECT60 = 50/50 blend at a high shear rate range. This result indicates that PECT blends containing BPC have better processability than those containing PC.

Summary

The miscibility of BPC/PECT blends was examined to develop blends having optical-grade clarity and better processability than PC/PECT blends. BPC/PECT blends, which are not miscible at a low temperature regardless of copolyester composition, become miscible upon heating because of UCST-type phase behavior when PECT copolyesters contain CHDM from 32 to 80 mole%. The homogenization temperature of blends decreased with CHDM content in PECT copolyester. The phase homogenization of BPC/PECT 5 blends was not observed until thermal degradation temperature (~330 °C). To understand the observed phase behavior, interaction energies of BPC/PECT blends were determined from the phase homogenization temperatures using the lattice-fluid theory, and then phase stability condition were explored. Interaction energies of PC-PECT pairs were positive and increased in the order of BPC-PECT80 < BPC-PECT60 < BPC-PECT32. Based on the analysis of phase stability condition, phase homogenization of these blends upon heating stemmed from combinatorial entropy term. By blending BPC and PECT, a novel blend, which overcomes drawbacks of PC and PECT and has better processability than PC/PECT blend, can be developed.

References

(1) D. Freitag, U. Grigo, P. R. Muller, and W. Nouvertne, *Polycarbonates in Encyclopedia of Polymer Science and Engineering*, H. F. Mark, N. M. Bikales, C. G. Overberger, and G. Menges, Eds., 2nd ed., John Wiley & Sons, 1985, Vol. 11, p 648.

(2) R. N. Mohn, D. R. Paul, J. W. Barlow, and C. A. Cruz, *J. Appl. Polym. Sci.*, **23**, 575 (1979).

(3) T. R. Nassar, D. R. Paul, and J. W. Barlow, *J. Appl. Polym. Sci.*, **23**, 85 (1979).

(4) C. A. Cruz, D. R. Paul, and J. W. Barlow, *J. Appl. Polym. Sci.*, **23**, 589 (1979).

(5) C. A. Cruz, D. R. Paul, and J. W. Barlow, *J. Appl. Polym. Sci.*, **23**, 2101 (1979).

(6) C. A. Cruz, D. R. Paul, and J. W. Barlow, *Macromolecules*, **12**, 726 (1979).

(7) W. A. Smith, J. W. Barlow, and D. R. Paul, *J. Appl. Polym. Sci.*, **26**, 4233 (1981).

(8) R. Murff, J. W. Barlow, and D. R. Paul, *J. Appl. Polym. Sci.*, **29**, 3231 (1984).

(9) J. M. Jonsa and R. S. Porter, *Macromolecules*, **19**, 1946 (1986).

(10) C. H. Lai, J. W. Barlow, and D. R. Paul, *Macromolecules*, **22**, 374 (1989).

(11) T. S. Ellis, *Macromolecules*, **28**, 1882 (1995).

(12) W. Brostow, M. Hess, B. L. Lopez, and T. Sterzynski, *Polymer*, **37**, 1551 (1996).

(13) V. N. Ignatov, C. Carraro, V. Tartari, R. Pippa, M. Scapin, F. Pilati, C. Berti, M. Tosseli, and M. Fiorini, *Polymer*, **38**, 195 (1997).

(14) V. N. Ignatov, C. Carraro, V. Tartari, R. Pippa, M. Scapin, F. Pilati, C. Berti, M. Tosseli, and M. Fiorini, *Polymer*, **38**, 201 (1997).

(15) G. Montaudo, C. Poglisi, and F. Samperi, *Macromolecules*, **31**, 650 (1998).

(16) T. S. Ellis, *Polymer*, **39**, 4741 (1998).

(17) Y. Kong and J. N. Hay, *Polymer*, **43**, 1805 (2002).

(18) C. K. Samios and N. K. Kalfoglou, *Polymer*, **41**, 5759 (2000).

(19) V. S. Shah, D. R. Paul, and J. W. Barlow, *J. Appl. Polym. Sci.*, **32**, 3863 (1986).

(20) D. R. Paul and J. W. Barlow, in *Polymer Science and Technology, Polymer Alloys II*, D. Klempner and K. C. Frisch, Eds., Plemum Press, New York, 1977, Vol. 11, p 239.

(21) S. Spall, A. A. Goodwin, M. D. Zipper, and G. P. Simon, *J. Polym. Sci.; Part B*, **34**, 2419 (1996).

(22) A. K. Kalkar, A. A. Deshpande, and M. J. Kulkarni, *J. Appl. Polym. Sci.*, **106**, 34 (2007).

(23) J. K. Lee, J. E. Im, J. W. Park, H. Y. Won, and K. H. Lee, *J. Appl. Polym. Sci.*, **99**, 2220 (2006).

(24) B. Yin, Y. Zhao, W. Yang, M. Pan, and M. Yang, *Polymer*, **47**, 8237 (2006).

(25) L. W. Kim, M. Y. Jeon, and C. K. Kim, *Ind. Eng. Chem. Res.*, **45**, 8921 (2006).

(26) J. H. Kim, M. S. Hwang, and C. K. Kim, *Macromolecules*, **37**, 2287 (2004).

(27) C. K. Kim and D. R. Paul, *Polymer*, **33**, 4929 (1992).

(28) M. Nishimoto, H. Keskkula, and D. R. Paul, *Polymer*, **32**, 272 (1991).

(29) T. A. Callaghan and D. R. Paul, *J. Polym. Sci.; Part B*, **32**, 1813 (1994).

(30) J. H. Kim, J. E. Yoo, and C. K. Kim, *Macromol. Res.*, **10**, 209 (2002).

(31) J. E. Yoo, Y. Kim, C. K. Kim, and J. W. Lee, *Macromol. Res.*, **11**, 303 (2003).

(32) I. C. Sanchez and R. H. Lacombe, *J. Phys. Chem.*, **80**, 2568 (1976).

(33) I. C. Sanchez and R. H. Lacombe, *J. Phys. Chem.*, **80**, 2352 (1976).

(34) I. C. Sanchez and R. H. Lacombe, *Macromolecules*, **11**, 1145 (1978).

(35) I. C. Sanchez and I. C. Polymer, *Phase Separation in Encyclopedia of Physical Science and Technology*, Academic Press Academic Press, New York, 1987, Vol. XI, p 1.

(36) G. R. Brannock and D. R. Paul, *Macromolcules*, **23**, 5240 (1990).