

Miscibility and Phase Behavior in Blends Containing Random Copolymers of Poly(ether ether ketone) and Phenolphthalein Poly(ether ether ketone)

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SYNOPSIS

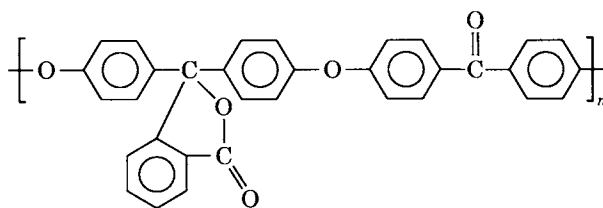
The miscibility and phase behavior of polysulfone (PSF) and poly(hydroxyether of bisphenol A) (phenoxy) with a series of copoly(ether ether ketone) (COPEEK), a random copolymer of poly(ether ether ketone) (PEEK), and phenolphthalein poly(ether ether ketone) (PEK-C) was studied using differential scanning calorimetry. A COPEEK copolymer containing 6 mol % ether ether ketone (EEK) repeat units is miscible with PSF, whereas copolymers containing 12 mol % EEK and more are not. COPEEK copolymers containing 6 and 12 mol % EEK are completely miscible with phenoxy, but those containing 24 mol % EEK and more are immiscible with phenoxy. Moreover, a copolymer containing 17 mol % EEK is partially miscible with phenoxy; the blends show two transitions in the midcomposition region and single transitions at either extreme. Two T_g s were observed for the 50/50 blend of phenoxy with the copolymer containing 17 mol % EEK, whereas a single composition-dependent T_g appeared for all the other compositions. An FTIR study revealed that there exist hydrogen-bonding interactions between phenoxy and the copolymers. The strengths of the hydrogen-bonding interactions in the blends of the COPEEK copolymers containing 6 and 12 mol % EEK are the same as that in the phenoxy/PEK-C blend. However, for the blends of copolymers containing 17, 24, and 28 mol % EEK, the hydrogen-bonding interactions become increasingly unfavorable and the self-association of the hydroxyl groups of phenoxy is preferable as the content of EEK units in the copolymer increases. The observed miscibility was interpreted qualitatively in terms of the mean-field approach. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

The use of polymer blends is becoming more and more important in specific sectors of the polymer industry because of strong economic incentives.¹⁻³ Although it is not always the most efficient, blending is the least expensive and most versatile technique to produce new materials from existing commodity polymers. Consequently, their attractiveness increases with the increasing demands for materials of this class.

Phenolphthalein poly(ether ether ketone) (PEK-C) is a novel high performance thermoplastic devel-

oped by these laboratories⁴ that is now commercially available in China. The repeat unit of PEK-C is

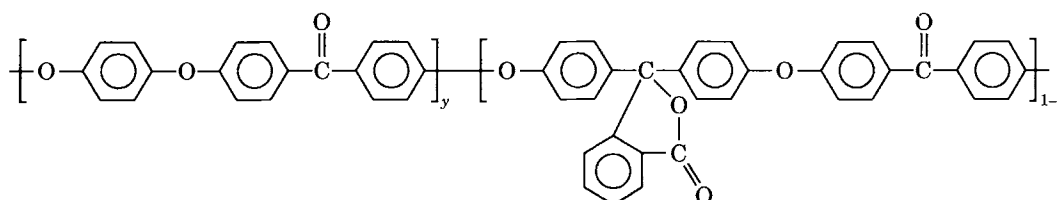


Its glass transition temperature (T_g) is ca. 228°C by differential scanning calorimetry (DSC); it is an amorphous polymer with mechanical properties comparable to the poly(ether ether ketone) (PEEK) developed by Imperial Chemical Ind., Ltd.,^{5,6} but has better electric properties. Because PEK-C is rela-

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tively lower in price than PEEK, considerable attention has been given to it as a high-performance thermoplastic as well as a matrix for advanced composites.⁷ PEK-C was also used to toughen epoxy resins.^{8,9}

Recently, much work has been done on blends of PEK-C with other polymers. These studies involved miscibility and properties of blends of PEK-C with polysulfone (PSF),^{10,11} poly(hydroxether of bis-



The techniques employed included DSC for glass transition behavior and Fourier-transform infrared spectroscopy (FTIR) for hydrogen-bonding interactions between the components of phenoxy/CO-PEEK blends.

EXPERIMENTAL

Materials and Preparation of Blends

The PEK-C sample with a reduced viscosity, η_{sp}/C , of 0.66 dL/g as a 0.5 wt % solution in chloroform at 25°C, was a commercial product of Xuzhou Engineering Plastics Factory, Xuzhou, Jiangsu, China. The phenoxy resin and PSF with weight-average molecular weights, M_w , of 43,000 and 59,000, respectively, were obtained from Guangzhou Chemical Factory, Guangzhou, Guangdong, China.

The COPEEK copolymers were synthesized by condensation of appropriate proportions of phenolphthalein, hydroquinone, and 4,4'-dichlorobenzophenone in the presence of potassium carbonate with sulfolane as solvent. They were prepared under nitrogen atmosphere first at 160–170°C for 2 h and further at 220°C for 8–12 h. Then it was diluted with *N,N*-dimethylformamide at 150°C and was precipitated in ethanol when cooled to room temperature. The precipitate was extracted by ethanol for 24 h and further washed in boiling distilled water. It was dried in a vacuum at 150°C to remove residual solvent. The synthesis was described in detail elsewhere.¹⁷ Some characteristics of the copolymers are listed in Table I. Chloroform was AR grade and was used as received.

All the blends were prepared by solution casting from chloroform. Solvent was allowed to evaporate slowly at room temperature. The blends were then

phenol A) (phenoxy),¹⁰ poly(ethylene oxide),¹² poly(*N*-vinyl-2-pyrrolidone),¹³ poly(2,6-dimethyl-1,4-phenylene oxide),¹⁴ PEEK,¹⁵ and a poly(ether imide).¹⁶

In this contribution, we are concerned with the miscibility and phase behavior of blends of PSF and phenoxy with a copoly(ether ether ketone) (CO-PEEK), a random copolymer of PEEK, and PEK-C. The schematic structure of COPEEK is shown below:

dried in a vacuum oven at room temperature for 2 weeks and at 60°C for 48 h.

DSC

The calorimetric measurements were made on a Perkin-Elmer DSC-7 differential scanning calorimeter in a dry nitrogen atmosphere. The instrument was calibrated with indium and zinc standards for low and high temperature regions, respectively. The sample weight used in the DSC cell was kept in the 8–12 mg range. The midpoint of the slope change of the heat capacity plot of the second scan was taken as glass transition temperature (T_g). A heating rate of 20°C/min was used.

IR Spectroscopy

A Perkin-Elmer 580B FTIR spectrometer was used to study hydrogen bonding interaction. All spectra

Table I Characteristics of Polymers Used

Sample	EEK in Copolymer ^a (mol %)	M_w ^b	η_{sp}/C^c (dL/g)	T_g^d (°C)
PSF		59,000		185
Phenoxy		34,000		96
PEK-C			0.66	228
COPEEK 6	6.2		0.73	222
COPEEK 12	12.3		0.77	218
COPEEK 17	16.7		0.70	213
COPEEK 24	23.5		0.74	210
COPEEK 28	27.8		0.67	204

^a By IR analysis.

^b Determined by GPC.

^c Measured on 0.5 wt % chloroform at 25°C.

^d By DSC.

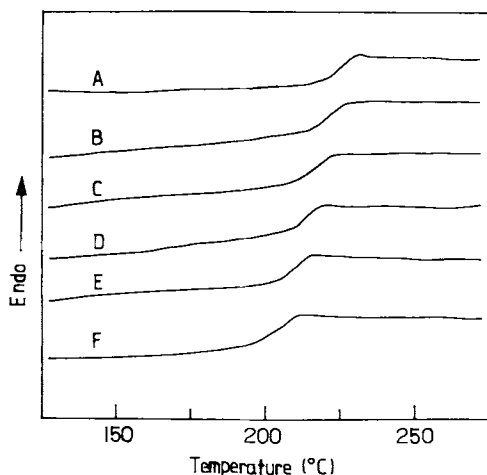


Figure 1 DSC thermograms of PEK-C and various COPEEK copolymers: (A) PEK-C, (B) COPEEK6, (C) COPEEK12, (D) COPEEK17, (E) COPEEK24, and (F) COPEEK28.

were recorded at room temperature. A minimum of 30 scans at a resolution of 3 cm^{-1} were signal averaged. The blend films used in this study were cast from chloroform and they were sufficiently thin to be within the absorption range where the Beer-Lambert law is obeyed.¹⁸

RESULTS AND DISCUSSION

COPEEK Copolymers

PEEK is a semicrystalline thermoplastic polymer with a T_g of 145°C and a melting point of the main crystallites around 340°C , depending on the thermal history.^{5,6} PEK-C on the contrary is an amorphous polymer with a high T_g of 228°C ; it has excellent mechanical properties comparable to PEEK. Figure 1 shows DSC thermograms of COPEEK copolymers and PEK-C. It can be seen from the figure that no crystallization peak was observed for COPEEK6, COPEEK12, COPEEK17, COPEEK24, and COPEEK28, indicating that the COPEEK copolymers containing EEK units up to 28 mol % are uncrystallizable although PEEK is crystalline. All of them are amorphous as well as PEK-C and show one single T_g dependent on copolymer composition. The T_g values of the copolymers are presented in Table I. It is to be noted that the T_g decreases with the content of EEK unit in the copolymer; this is because T_g of PEEK (145°C) is lower than that of PEK-C (228°C).

PSF/COPEEK Blends

The miscibility of PSF/PEK-C blends was established in the previous study.^{10,11} In the present case, all the PSF/COPEEK6 blends were transparent and each blend showed only one T_g , but the blends of PSF with COPEEK12, COPEEK17, and COPEEK28 were opaque and had two T_g s. Figure 2 presents T_g as a function of blend composition for blends of PSF with various COPEEK copolymers. It can be seen that the PSF/COPEEK6 blend has a single, composition-dependent T_g [Fig. 2(A)], indicating its single-phase nature. Thus, PSF is miscible with COPEEK6 over the entire composition range. The T_g data for the blends as shown in Figure 2(A) can be described by the use of Gordon-Taylor equation¹⁹

$$T_g = (w_1 T_{g1} + k w_2 T_{g2}) / (w_1 + k w_2) \quad (1)$$

Here, T_g is the glass transition temperature of the blend, whereas T_{g1} and T_{g2} are the glass transition temperatures of component 1 and component 2, respectively, w is the weight fraction, and k is a constant. The curve in Figure 2(A) is drawn using the Gordon-Taylor equation with a k value of 0.38, fitting the experimental data well.

Belorgey et al. suggested²⁰⁻²² that the k value can be taken as a semiquantitative measure of the strength of interaction between the components of the blend. For instance, in blends of poly(ϵ -caprolactone) with chlorinated polyethylene, poly(vinyl chloride) (PVC), and chlorinated PVC, k increases from 0.26 to 1.0. When such an approach is used for the PSF/COPEEK6 blends, we note that the k value

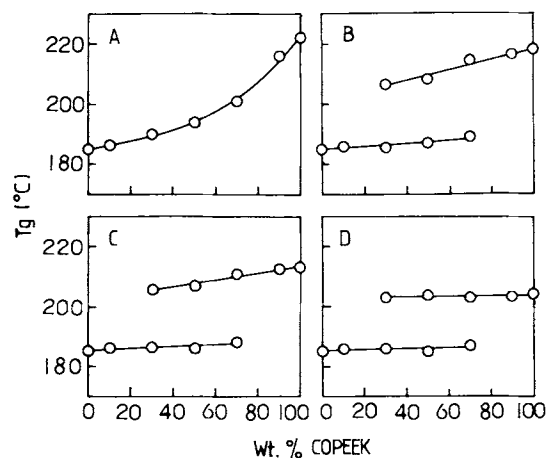


Figure 2 Glass transition temperatures for blends of PSF with various COPEEK copolymers: (A) COPEEK6, (B) COPEEK12, (C) COPEEK17, and (D) COPEEK28.

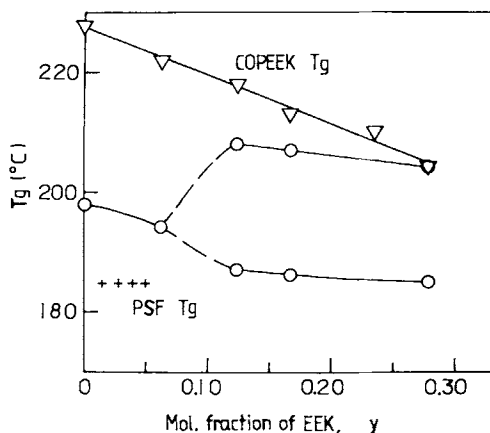


Figure 3 Dependence of the glass transition temperature of the 50/50 PSF/COPEEK blend on copolymer composition.

(0.38) is smaller than that (0.54) of the PSF/PEK-C blend previously obtained,¹⁰ suggesting that the interaction between PSF and COPEEK6 is weaker than that between PSF and PEK-C.

However, it can be seen from the figure that there exist two T_g s for all the PSF/COPEEK12, PSF/COPEEK17, and PSF/COPEEK28 blends; the T_g values obtained are close to those of their components, respectively. This obviously shows that the PSF is immiscible with COPEEK12, COPEEK17, and COPEEK28.

The T_g data of the 50/50 PSF/COPEEK blends are depicted in Figure 3 as a function of copolymer

composition. A COPEEK copolymer containing 6 mol % EEK has one single T_g and is miscible with PSF, whereas copolymers containing 12 mol % EEK and more possess two T_g s and are immiscible with PSF. It is reasonable to conclude from the figure that the critical value of y for miscibility is about 0.06.

Phenoxy/COPEEK Blends

Phenoxy has been proved to be miscible with PEK-C.¹⁰ All the phenoxy/COPEEK6 and phenoxy/COPEEK12 blends were transparent and each blend showed only one composition-dependent T_g as shown in Figure 4. These suggest that phenoxy is completely miscible with COPEEK6 and COPEEK12. The curves in Figure 4(A) and (B) are drawn by using the Gordon-Taylor equation with k values of 0.56 and 0.32, respectively. Both of them are smaller than that (0.87) previously obtained for the phenoxy/PEK-C blend system.¹⁰ This means that the overall interactions in both phenoxy/COPEEK6 and phenoxy/COPEEK12 blends are weaker than that in the phenoxy/PEK-C blend.

The transparency of the phenoxy/COPEEK17 blend films are dependent on composition. The T_g s of phenoxy/COPEEK17 blends as a function of blend composition are presented in Figure 4(C). It is interesting to see that the blends show two transitions in the midcomposition region and single transitions at either extreme. In the figure, two T_g s

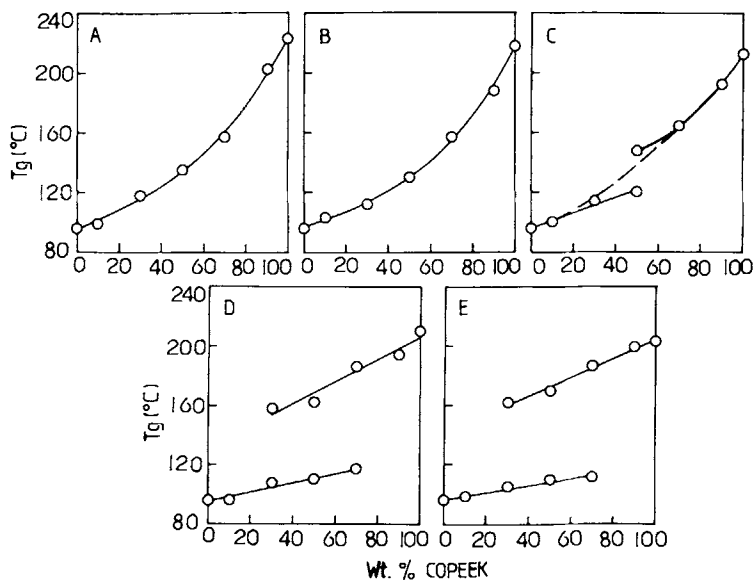


Figure 4 Glass transition temperatures for blends of phenoxy with various COPEEK copolymers: (A) COPEEK6, (B) COPEEK12, (C) COPEEK17, (D) COPEEK24, and (E) COPEEK28.

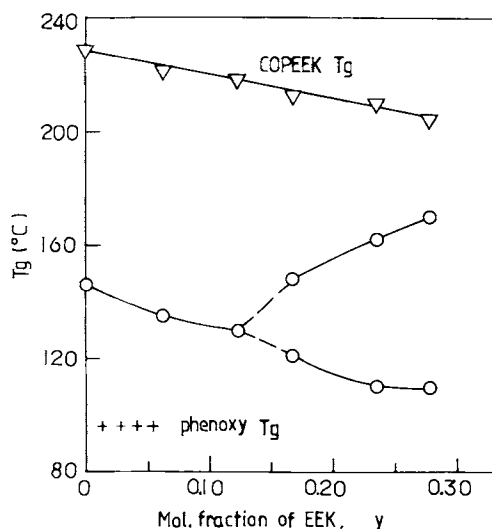


Figure 5 Dependence of the glass transition temperature of the 50/50 phenoxy/COPEEK blend on copolymer composition.

are observed only for the 50/50 phenoxy/COPEEK17 blend, whereas a single composition-dependent T_g is presented for all the other compositions. It can be considered that phenoxy is partially miscible with COPEEK17.

Not all of the films of the phenoxy/COPEEK24 and phenoxy/COPEEK28 blends were clear. Figure 4 also shows T_g -composition dependence of phenoxy/COPEEK24 and phenoxy/COPEEK28 blends. Two T_g s are observed in the figure for each of the two blends. It is quite evident that these blends are immiscible.

The T_g data of the 50/50 phenoxy/COPEEK blends are depicted in Figure 5 as a function of copolymer composition. It is obvious that COPEEK copolymers containing 6 and 12 mol % EEK are completely miscible with phenoxy, whereas those containing 17 mol % EEK and more are not. We can conclude from the figure that the critical value of y for miscibility is about 0.12.

Although phenoxy strongly self-associates because of its pendant hydroxyl, it has excellent potential for hydrogen bonding as a proton donor. Phenoxy has been proved to be miscible with many proton-acceptor polymers, including poly(vinyl pyrrolidone),²³ poly(ether sulfone),²⁴ and several polyesters and polyethers.²⁵⁻³⁰ Coleman and Moskala^{29,30} proved that there are hydrogen-bonding interactions involving the phenoxy hydroxyl groups and either the carbonyl or the ether oxygen moieties of the other polymers. The hydrogen-bonding interactions between phenoxy and PEK-C was revealed by a FTIR study in the previous work.¹⁰

Figure 6 shows IR spectra in the 3,000–4,000 cm^{-1} region of pure phenoxy and 50/50 blends of phenoxy with COPEEK6, COPEEK12, COPEEK17, COPEEK24, and COPEEK28, all recorded at room temperature. As shown by Coleman and Moskala,²⁹ the spectrum in this region of pure phenoxy may be considered to be composed of two components: a broad band centered at 3400 cm^{-1} attributed to hydrogen-bonded hydroxyl groups (self-associated) and a relatively narrow band at 3570 cm^{-1} assigned to free (nonassociated) hydroxyl groups. Our previous work¹⁰ showed that upon mixing with PEK-C, the broad hydrogen-bonded hydroxyl band of the phenoxy shifts to higher frequencies as a function of increasing PEK-C concentration, indicating that the hydrogen-bonding interaction between hydroxyl groups of phenoxy and PEK-C is presented and its strength is weaker than that in pure phenoxy. For the 50/50 phenoxy/PEK-C blend, the broad hydrogen-bonded hydroxyl band of the phenoxy was observed to be centered at 3460 cm^{-1} .¹⁰ It can be seen from Figure 6 that for the 50/50 blends of phenoxy with COPEEK6 and COPEEK12, the broad hydrogen-bonded hydroxyl band of the phenoxy remains centered at 3460 cm^{-1} , the same as that for the 50/50 phenoxy/PEK-C blend. This implies

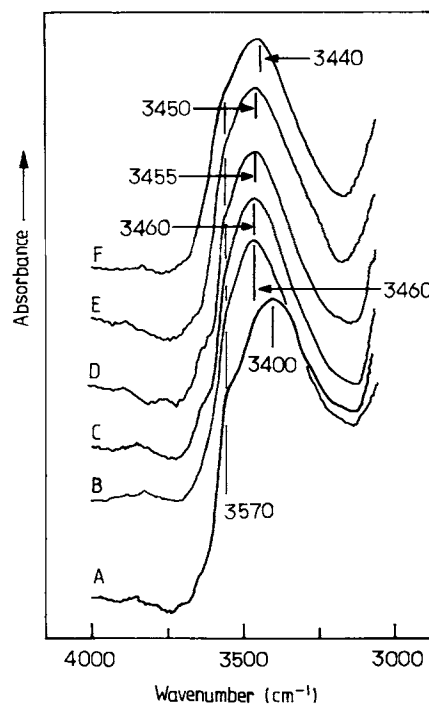


Figure 6 FTIR spectra of the region from 3,000 to 4,000 cm^{-1} recorded at room temperature of (A) pure phenoxy and of the 50/50 phenoxy blends with (B) COPEEK6, (C) COPEEK12, (D) COPEEK17, (E) COPEEK24, and (F) COPEEK28.

that hydrogen-bonding interactions exist between phenoxy and the two copolymers with the same strength as that in the phenoxy/PEK-C blend.

However, it is to be noted that for the 50/50 blends of phenoxy with COPEEK17, COPEEK24, and COPEEK28, the broad hydrogen-bonded hydroxyl band of the phenoxy is observed to shift back to lower frequencies with increasing EEK unit content in the copolymer. Peaks are observed at 3455, 3450, and 3440 cm^{-1} , respectively, in Figure 6 for the 50/50 blends of phenoxy with COPEEK17, COPEEK24, and COPEEK28. This observation suggests that the hydrogen-bonding interactions between phenoxy and COPEEK copolymers become increasingly unfavorable and the self-associations of the hydroxyl groups of phenoxy become preferable as the content of EEK unit in the copolymer increases, in accordance with the results obtained above by DSC that phenoxy is not completely miscible with these three copolymers.

Interpretation

Miscibility of polymer blends containing copolymers can be described by using the mean-field approach.³¹ The overall interaction energy density, B_{blend} , between the two polymers can be simply expressed in terms of the binary interaction energy densities, B_{ij} .

In binary mixtures of a homopolymer A with a random copolymer $C_y D_{1-y}$, where y represents the mole fraction of C units in the copolymer, the blend interaction energy density B_{blend} is given by the following expression³²⁻³⁴:

$$B_{\text{blend}} = yB_{AC} + (1 - y)B_{AD} - y(1 - y)B_{CD} = f(y) \quad (2)$$

For infinite molecular weight polymers, phase separation occurs when $f(y) = 0 = B_{\text{crit}}$.

Application of eq. (2) to the understanding of the phase behavior of copolymer mixtures has met with great success. In the present case, because the binary interaction energy densities B_{ij} are not available and are difficult to estimate, it is impossible to quantitatively analyze both the PSF/COPEEK and phenoxy/COPEEK blends. However, the miscibility and phase behavior observed can be qualitatively interpreted.

For the PSF/COPEEK and phenoxy/COPEEK blends, PSF and phenoxy are homopolymers, A , whereas the EEK units and the repeat units of PEK-C in the COPEEK copolymers are designated as C and D , respectively. First, PEK-C is miscible with

both PSF and phenoxy over the entire temperature range,¹⁰ then the B_{AD} values for both the PSF/COPEEK and phenoxy/COPEEK blends are negative. Second, the B_{CD} values for the two blends are the same and should be positive because PEEK is not miscible with PEK-C.¹⁵ It is also interesting to see from Figures 3 and 5 that only one miscibility limit exists for both blend systems. The critical copolymer composition y for achieving miscibility with PSF has been estimated to be about 0.06 and that with phenoxy about 0.12. These results, in light of eq. (2), clearly indicates that the B_{AC} values for the PSF/COPEEK and phenoxy/COPEEK blends should be positive, that is, neither PSF nor phenoxy is miscible with PEEK. Furthermore, we note that the critical value of y for miscibility with phenoxy is larger than that with PSF, which is in agreement with the fact that there are hydrogen-bonding interactions between phenoxy and PEK-C as well as between phenoxy and copolymers. Besides, it is worth noting that the critical values of y for miscibility with PSF and phenoxy are rather low, implying that the miscibility of PSF and phenoxy with COPEEK copolymers is mainly due to the negative B_{AD} value, that is, the contribution of favorable interactions of PSF and phenoxy with the repeat units of PEK-C in the copolymers, while the repulsion between the EEK units and the repeat units of PEK-C in the copolymers contributes rather little to the miscibility.

CONCLUSIONS

From the results presented in this article it can be concluded that the miscibility of COPEEK copolymers with PSF and phenoxy is dependent on copolymer composition. PSF exhibits miscibility with COPEEK6, but it is immiscible with COPEEK12, COPEEK17, and COPEEK28. Phenoxy is completely miscible with both COPEEK6 and COPEEK12, but it is immiscible with COPEEK24 and COPEEK28. The phenoxy/COPEEK17 blends are partially miscible. The blends show two transitions in the midcomposition region and single transitions at either extreme. Two T_g s were observed for the 50/50 phenoxy/COPEEK17 blend, whereas a single composition-dependent T_g appeared for all other compositions. An FTIR study revealed that hydrogen-bonding interactions exist between phenoxy and the copolymers. The strengths of the hydrogen-bonding interactions in both the phenoxy/COPEEK6 and phenoxy/COPEEK12 blends are the same as that in the phenoxy/PEK-C blend.

However, for the phenoxy blends with COPEEK17, COPEEK24, and COPEEK28, the hydrogen-bonding interactions between the components become increasingly unfavorable; and the self-association of the hydroxyl groups of phenoxy is preferable with an increase of the EEK content in the copolymer. The observed miscibility was interpreted qualitatively in terms of mean-field approach.

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