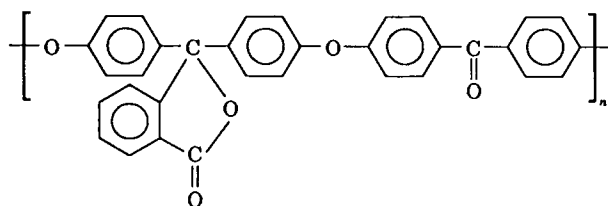


NOTE

The Phase Behavior of Phenolphthalein Poly(ether Ether Ketone) with Poly(ethylene Oxide)

INTRODUCTION

Phenolphthalein poly(ether ether ketone) (PEK-C) with structural formula



and $T_g = 228^\circ\text{C}$ is an amorphous high performance thermoplastic developed by this laboratory.¹ It can be used also as a matrix for advanced composites. Recently, considerable attention has been devoted to blends of PEK-C with other thermoplastics. In a previous work,² we have established the miscibility of PEK-C with poly(hydroxy ether) of bisphenol A (phenoxy) and polysulfone (PSF). In this, the miscibility and phase behavior of PEK-C with poly(ethylene oxide) (PEO) is reported.

EXPERIMENTAL

The PEK-C ($\bar{M}_n = 12,000$) was commercially obtained from Xuzhou Chemical Factory, Xuzhou, China. It has a density of 1.309 g/cm^3 and a glass transition temperature (T_g) of 228°C . Four samples of PEO were supplied by Shanghai Chemical Factory, Shanghai, China. They are: PEO1000, PEO6000, PEO20,000, and PEO200,000 with weight-average molecular weight 1000, 6000, 20,000, and 200,000, respectively. Chloroform was AR grade and was used as received.

The blends were prepared by solution casting from chloroform. Solvent was allowed to evaporate slowly at room temperature. To remove the residual solvent, the samples were then dried in a vacuum oven at 50°C for approximately 4 weeks.

The cloud point curves for the PEK-C/PEO systems were determined using an Olympus optical microscope fitted with a hot stage. The blend film was sandwiched between two microscope cover glasses and heated at a rate of about $20^\circ\text{C}/\text{min}$. The opaque film first became clear, indicating the melting of the PEO, and then again became cloudy with increasing temperature. The temperature at which the first faint opalescence, after the melting of the PEO, appeared on heating was designated as the cloud point. Observed melting points of several standard compounds using this method checked closely with published values.

A Perkin-Elmer DSC-2C differential scanning calorimeter was used to examine the melting behavior of the PEK-C/PEO blends with high PEO contents at a heating rate of $20^\circ\text{C}/\text{min}$. The temperature of the peak of the melting endotherm from DSC was taken as the melting point (T_m).

RESULTS AND DISCUSSION

All the blends were found to undergo phase separation. The cloud point curves are shown in Figure 1. An increase in the molecular weight of the PEO decreases the cloud point temperature as expected. The minimum in the cloud point curve appears close to a 20/80 PEK-C/PEO ratio. The change of this composition with molecular weight of PEO causes the curves to cross. However, this composition varies relatively rather little with molecular weight, as the molecular weight of PEO is varied from almost an order of magnitude lower than that of PEK-C to an order of magnitude higher. The skew nature of these curves thus must be due little to molecular weight effects but mainly to, for example, differences between the equation of state properties of the base polymers. This could be due to differences in the thermal expansion coefficients, thermal pressure coefficients, or surface areas per unit volumes of the two polymers, as have been described by other authors.³⁻⁷

Melting point temperatures, T_m , for the PEK-C/PEO blends optical measurements agree closely with the temperatures of the peak of the melting endotherm from DSC (Fig. 2). The melting point depression was small. For a miscible polymer blend containing a crystallizable component, the melting point depression of crystalline polymer

by the miscible diluent is frequently used to calculate the interaction parameter B using the equation^{8,9}

$$T_m = T_{m0} + B(V_{2u}/\Delta H_{2u})T_{m0}\phi_1^2 \quad (1)$$

where T_{m0} and T_m are the melting points of pure PEO and PEO in the blend respectively, ϕ_1 is the volume fraction of PEK-C in the blends, and $\Delta H_{2u}/V_{2u}$ characterizes the heat of fusion per unit volume for 100% crystalline PEO. The latter was computed from the following literature values¹⁰: $V_{2u} = 38.9 \text{ cm}^3/\text{mol}$ and $\Delta H_{2u} = 2100 \text{ cal/mol}$. From the plot of T_m against ϕ_1^2 (Fig. 2), B was found to be -1.66 , -1.55 , -1.38 , and -1.03 cal/cm^3 for PEK-C/PEO1000, PEK-C/PEO6000, PEK-C/PEO20,000, and PEK-C/PEO200,000 blend systems, respectively. The lower molecular weight of PEO, the more negative B value of the blend. This is in agreement with the observed cloud point behavior. It has been shown that the cloud point increases as the interaction parameter B becomes more negative.¹¹ As the morphological effect on the melting point depression of PEO has not been separated out, the estimates for B may be subject to some errors, especially for the blend systems with PEO of higher molecular weights (PEO20,000 and PEO200,000). Consequently, we can attach very little significance to the absolute value B except to say that it appears to be negative, which is in agreement with the observed, limited, miscibility of the two polymers.

T_g measurement has usually been used to determine miscibility in blends. Unfortunately, for the PEK-C/PEO systems of this study there was no real evidence for a transition of this type by DSC. The T_g of the plain PEK-C was 501 K. Inserting this value into Fox equation,¹² together with a value of 200 K for the T_g of PEO,⁶ indicates

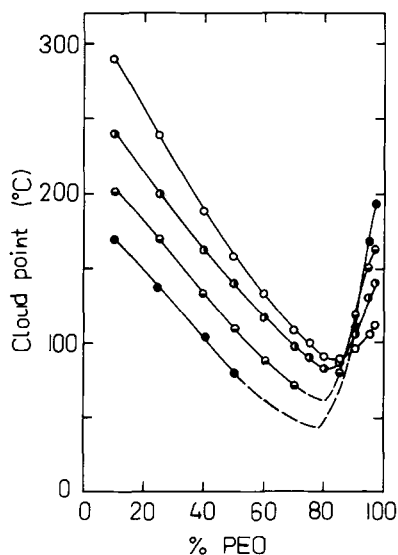


Figure 1 Plot of cloud points against composition for PEK-C blends with PEO1000 (O), PEO6000 (●), PEO20,000 (◐), and PEO200,000 (◑).

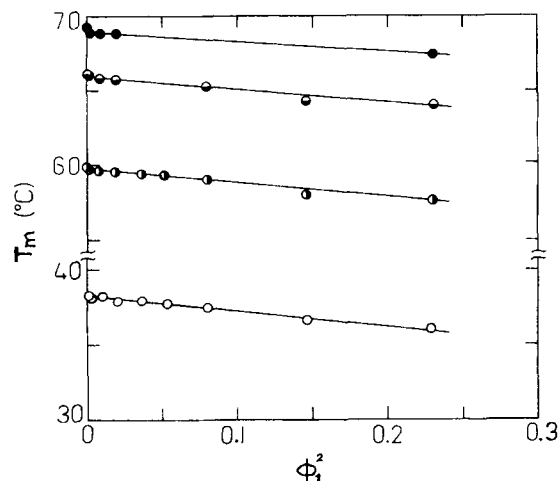


Figure 2 Melting points of PEK-C blends with PEO1000 (O), PEO6000 (◐), PEO20,000 (◑), and PEO200,000 (●).

that in the high PEK-C content range the blend T_g could be expected to be in the same temperature range as the corresponding cloud point, and so it is difficult to experimentally determine the T_g values. A similar result for both polysulfone/PEO and poly(ether sulfone)/PEO blend system was noted by Walsh et al.^{3,6}

CONCLUSION

It could be shown that PEO has limited miscibility with PEK-C. With relatively low molecular weight PEO1000 and PEO6000, clear, homogeneous films were obtained for all compositions and for temperatures between the melting point of the PEO in the blends and the cloud point; with the higher molecular weight PEO20,000 and PEO200,000, homogeneous blends were obtained only with high PEK-C contents. The temperature of phase separation is lowered with increase of PEO molecular weight. The minimum in the cloud point curve for the four PEK-C/PEO blend systems all appears to occur around 75–85 wt % of PEK-C. The values of interaction parameter B were estimated from the melting point depressions of the PEO. The more negative B value for the lower molecular weight PEO is in agreement with the observed cloud point behavior of the PEK-C/PEO blend systems. The T_g for the homogeneous PEK-C/PEO blends is predicted to occur in the same temperature range as that of the cloud point for low PEO contents making experimental determination difficult.

References

1. H. Zhang and T. Chen, Chin. Pat. 85108751 (1985).
2. Q. Guo, J. Huang, and T. Chen, *Polym. Bull.*, **20**, 517 (1988).

3. B. T. Swingyard, J. A. Barrie, and D. J. Walsh, *Polym. Commun.*, **28**, 331 (1987).
4. L. P. McMaster, *Macromolecules*, **6**, 760 (1973).
5. O. Olabisi, *Macromolecules*, **8**, 316 (1975).
6. D. J. Walsh and V. B. Singh, *Makromol. Chem.*, **185**, 1978 (1984).
7. D. J. Walsh, S. Rostami, and V. B. Singh, *Makromol. Chem.*, **186**, 145 (1986).
8. T. Nishi and T. T. Wang, *Macromolecules*, **8**, 909 (1975).
9. R. L. Imken, D. R. Paul, and J. W. Barlow, *Polym. Eng. Sci.*, **16**, 593 (1976).
10. D. W. Krevelen, *Properties of Polymers*, 2nd ed., Elsevier, Amsterdam, 1976.
11. D. R. Paul, J. W. Barlow, R. E. Bernstein, and D. C. Wahrmund, *Polym. Eng. Sci.*, **18**, 1225 (1978).
12. T. G. Fox, *Bull. Am. Phys. Soc.*, **1**, 123 (1956).

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