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A closed-loop phase behaviour of ternary homopolymer blend composed of three miscible binaries

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The phase behaviour of ternary polymer blend of poly(methyl methacrylate) (PMMA), poly(ethylene oxide) (PEO) and poly(hydroxy ether of bisphenol-A) (phenoxy) was investigated. Although all three binary blends are separately miscible, there exists a closed immiscibility loop in the phase diagram of ternary blends. It may result from small differences in the interaction energy of binary systems, the so-called '$\Delta\chi$ effect'. The value of $\chi_{\mathrm{phenoxy/PMMA}}$, by comparing the theoretically predicted phase diagram with experimental data, was determined to be −0.61. © 1997 Elsevier Science Ltd.

(Keywords: closed-loop; ternary blend; $\Delta\chi$ effect)

INTRODUCTION

Multicomponent polymer blends are of significant industrial importance and therefore it is very interesting to investigate the phase behaviour of ternary polymer blends. Since the early works of Scott and Tompa[1,2], most studies on ternary polymer blends have been developed with the concept that polymer A, which is miscible with each of polymers B and C, can compatibilize the immiscible binary pair B and C[3–7]. On the other hand, few studies of ternary polymer blends with all three binary pairs being miscible have been reported in the literature. When all three binary pairs are miscible, a completely homogeneous phase diagram is possible[8]. However, differences in the interaction energy of the binary systems, the so-called '$\Delta\chi$ effect', can result in phase separation[9,10]. As we have reported in our previous work[11], ternary poly(methyl methacrylate) (PMMA)/poly(ethylene oxide) (PEO)/poly(styrene-co-acrylic acid) blend shows such a closed loop of phase-separated region in the phase diagram. Recently, Rabeony *et al.*[12] also reported that ternary polystyrene/poly(2-chlorostyrene)/poly(cyclohexylacrylate) blend consisting of three pairwise miscible homopolymers shows a closed-loop immiscibility.

It has previously been reported that all three binary pairs of PMMA, PEO, and poly(hydroxy ether of bisphenol-A) (phenoxy) homopolymers are separately miscible[13–15]. In the present study, we have investigated the phase behaviour of ternary PMMA/PEO/phenoxy blends and determined the value of $\chi_{\mathrm{phenoxy/PMMA}}$ by comparing the theoretically predicted phase diagram with experimental data.

EXPERIMENTAL

PMMA ($M_w = 91\,380\,\mathrm{g\,mol^{-1}}$, $T_g = 101°\mathrm{C}$) was a commercial product supplied by the LG Chemical Ltd., Korea and PEO ($M_w = 105\,010\,\mathrm{g\,mol^{-1}}$, $T_m = 66°\mathrm{C}$, $T_g = -59°\mathrm{C}$) was purchased from the Aldrich Chemical Co., USA. Phenoxy ($M_w = 47\,540\,\mathrm{g\,mol^{-1}}$, $T_g = 86°\mathrm{C}$), obtained from the Union Carbide Co., USA, was a commercial product designated as phenoxy PKHH. The molecular weights of all samples were determined by g.p.c. All samples were dried in vacuum oven at 50°C for at least 5 days before blending and used without further purification. The polymer samples were melt-mixed and injection-moulded in a Mini-Max Moulder (CS-183 MMV, Custom Scientific Instruments, Inc., USA) at 170°C for 5 min. The thermal properties were measured using a Perkin–Elmer DSC-7 equipped with a mechanical cooling accessory. All scans were run under a nitrogen gas purge to minimize the oxidative degradation. For the measurement of glass transition temperature, blend samples were heated to 170°C at a heating rate of 20°C min^{-1}, maintained at 170°C for 5 min to ensure complete melting of PEO crystals, and then quenched to −90°C. They were then reheated to 170°C at a heating rate of 20°C min^{-1}.

RESULTS AND DISCUSSION

Figure 1 shows the composition dependence of the glass transition temperature of three binary blends. It is observed that d.s.c. thermograms of all three binaries exhibit single, composition-dependent T_g's, indicating that three binary blends are separately miscible.

Figure 2 shows five representative d.s.c. thermograms of ternary PMMA/PEO/phenoxy blends. The arrow

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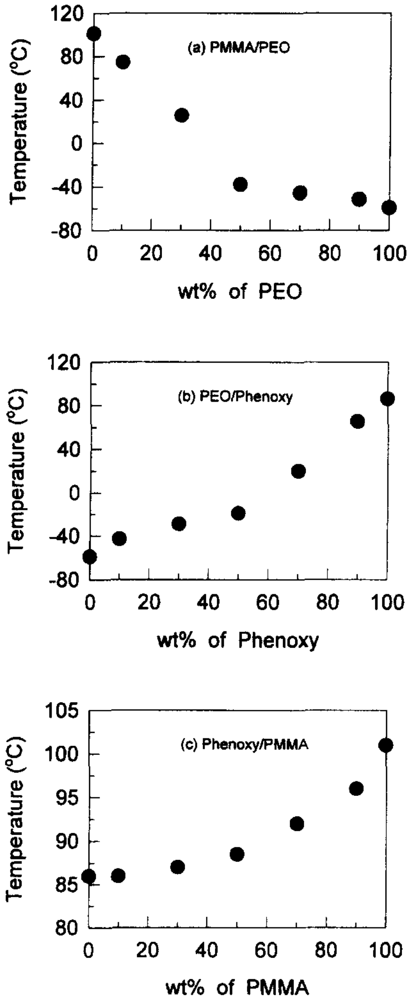

Figure 1 Composition dependence of the glass transition temperature of three binary blends: (a) PMMA/PEO; (b) PEO/phenoxy; (c) phenoxy/PMMA

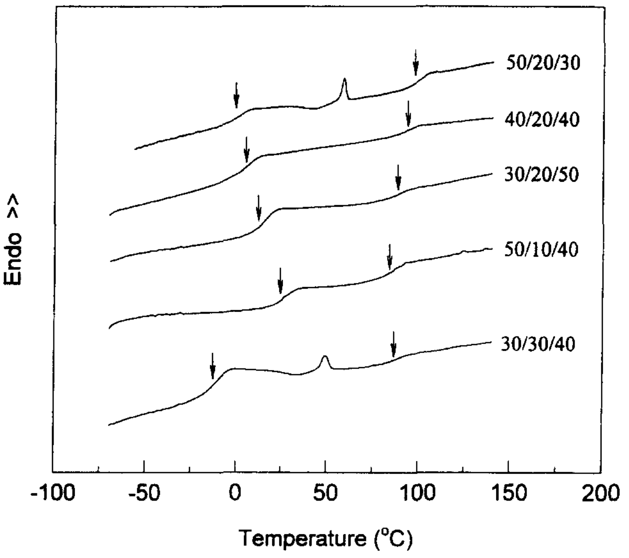

Figure 2 Selected d.s.c. thermograms for ternary blends of PMMA/PEO/phenoxy at various compositions. The arrow indicates the position of the glass transition temperature

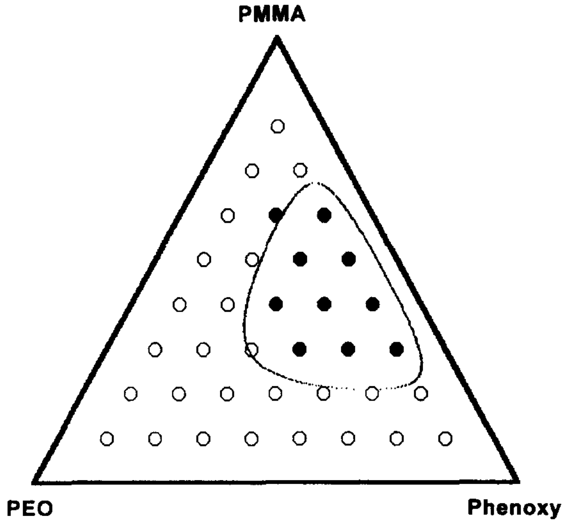

Figure 3 Phase diagram of ternary PMMA/PEO/phenoxy blend. The full circles represent compositions where two T_g's are observed and the open circles represent compositions where a single T_g is observed. The full curve is the spinodal calculated by equation (4) with $\chi_{PMMA/PEO} = -0.35$, $\chi_{PEO/phenoxy} = -1.90$, $\chi_{phenoxy/PMMA} = -0.61$, $m_{PMMA} = 914$, $m_{PEO} = 2387$, and $m_{phenoxy} = 167$

represents the position of the glass transition temperature. Although all three binary blends are miscible over the entire compositions, the ternary blends have clearly two T_gs at given compositions in *Figure 2*. This result indicates the immiscibility of ternary PMMA/PEO/phenoxy blends at these compositions.

Figure 3 shows the phase diagram of ternary PMMA/PEO/phenoxy blends. The ternary blends, showing a single T_g, were determined to be miscible, and those, exhibiting double T_g's, were determined to be immiscible. There exists a closed-loop of phase-separated region in the phase diagram. In the case of a ternary system consisting of two polymers and a solvent, small differences in the interaction energy of the binary systems, the so-called '$\Delta\chi$ effect', can result in phase separation although all three pairs are separately miscible[9,10]. Therefore the closed loop in the phase diagram of the present system may result from the '$\Delta\chi$ effect'. This phase behaviour can be theoretically predicted and compared with the experimental data. The spinodal analysis based on the Flory–Huggins theory has been used to reproduce the experimental miscibility boundary. Su and Fried[16] have mathematically computed spinodal curves using the Flory–Huggins lattice theory for different combinations of the binary interaction parameters to provide guidelines for miscibility in ternary polymer blends. The essential details are summarized below. The free energy of mixing (ΔG_m) of three monodisperse homopolymers may be given in terms of volume fractions (ϕ_i) as

$$\tilde{G} = \left(\frac{\Delta G_m}{kT}\right)\left(\frac{V_u}{V}\right) = \left(\frac{\phi_1}{m_1}\right)\ln\phi_1 + \left(\frac{\phi_2}{m_2}\right)\ln\phi_2 + \left(\frac{\phi_3}{m_3}\right)\ln\phi_3 + \chi_{12}\phi_1\phi_2 + \chi_{23}\phi_2\phi_3 + \chi_{31}\phi_3\phi_1 \qquad (1)$$

where V_u is the volume per lattice site, V is the mixture volume, m_i is the chain length of polymer i, and χ_{ij} is the Flory interaction parameter between segments of polymers i and j. The boundary condition for the spinodal is given by

$$G_{22}G_{33} - (G_{23})^2 = 0 \qquad (2)$$

where

$$G_{ij} = \left(\frac{\partial^2 \tilde{G}}{\partial\phi_i \partial\phi_j}\right)_{T,P} \tag{3}$$

From equations (1) and (2), the equation for the spinodal of a ternary blend is given by

$$\begin{aligned} &m_1\phi_1 + m_2\phi_2 + m_3\phi_3 - 2[m_1m_2(\chi_1 + \chi_2)\phi_1\phi_2 \\ &\quad + m_2m_3(\chi_2 + \chi_3)\phi_2\phi_3 + m_3m_1(\chi_3 + \chi_1)\phi_1\phi_3] \\ &\quad + 4m_1m_2m_3(\chi_1\chi_2 + \chi_2\chi_3 + \chi_3\chi_1)\phi_1\phi_2\phi_3 = 0 \end{aligned} \tag{4}$$

where

$$\chi_i = (\chi_{ij} + \chi_{ik} - \chi_{jk})/2 \tag{5}$$

To compare the experimental data with theoretical predictions, one must know the χ_{ij} values for each of the binary pairs in the system. The values of $\chi_{\mathrm{PMMA/PEO}}$ and $\chi_{\mathrm{PEO/phenoxy}}$ obtained from the literature[13,14] were −0.35 and −1.90, respectively. The phase diagram can be predicted from equation (4) with various values of $\chi_{\mathrm{phenoxy/PMMA}}$. When the value of $\chi_{\mathrm{phenoxy/PMMA}}$ is −0.61, as shown in *Figure 3*, the experimental data are best fit by the predicted spinodals. Therefore the value of $\chi_{\mathrm{phenoxy/PMMA}}$ was determined to be −0.61.

CONCLUSIONS

The phase behaviour of ternary PMMA/PEO/phenoxy blend was investigated by means of thermal analysis. Although all three binary pairs are separately miscible, there exists a closed immiscibility loop in the phase diagram of the ternary blend. It may result from the asymmetry in the interaction energy of binary systems, the so-called '$\Delta\chi$ effect'. The theoretical prediction based on the modified Flory–Huggins theory was compared with the experimental data and the value of $\chi_{\mathrm{phenoxy/PMMA}}$ was determined to be −0.61.

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