Amorphous polyurethane–polyether blends

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As we have reported recently, the application of association models has provided a theoretical basis for the calculation of the free energy changes and phase diagrams of binary polymer blends in which hydrogen bonding plays a significant role. Here we perform theoretical calculations of the phase diagrams of a number of amorphous polyurethane–polyether blends. The concordance between the theoretical predictions and gross experimental observations of the miscibility of these polymer blend systems is very encouraging.

(Keywords: binary polymer blends; hydrogen bonding; polyurethane; polyether)

INTRODUCTION

We recently published a paper pertaining to the mixing of a simple amorphous aromatic/aliphatic polyurethane (APU) with a poly(ethylene oxide-*co*-propylene oxide) (EPO) polymer[1]. This system was found to be miscible throughout the entire composition range at 110°C. A theory describing the free energy of mixing based upon a simple association model approach was presented[2]. This theory has now been extended to include calculations of the spinodal for binary polymer blends where one polymer self-associates through intermolecular hydrogen bonding while the second does not. The latter, nonetheless, is capable of forming a hydrogen bond with the former[3,4]. Theoretical calculations of the phase diagrams of a number of poly(4-vinyl phenol) (PVPh) blends with various polyacrylates, polyacetates and polyesters were performed and found to be in excellent agreement with experimental observations[5]. In this paper, we will turn our attention to APU blends with a number of polyethers. Frankly, due to the relatively high T_g of APU coupled with the unfortunate predisposition of both polymeric components to degrade at elevated temperatures, APU–polyether blends are not the type of systems that are usually considered for experimental studies of phase behaviour. A fascinating experimental observation, however, compels us to study these blends despite their limitations. APU–poly(ethylene oxide) and APU–EPO blends are miscible at 110°C while the corresponding APU–poly(vinyl methyl ether) blends are unequivocally immiscible. Based upon our experience of similar polymer mixtures, we were surprised by this result. Even more surprising, however, is that our theory, which contains no adjustable parameters, predicts such a result.

EXPERIMENTAL

The APU and EPO polymers have been described previously[1]. Poly(vinyl methyl ether) (PVME) was obtained from Polysciences Inc. and has a glass transition temperature of −27°C. Poly(ethylene oxides) (PEOs) of varying molecular weights were purchased from Scientific Polymer Products Inc.

Infra-red spectra were recorded on either Digilab Models FTS-15E or FTS-60 Fourier transform infra-red (*FT*i.r.) spectrometers at a resolution of $2\,\mathrm{cm}^{-1}$. A minimum of 64 scans were signal averaged, and the spectra were stored on a magnetic disc system. Spectra recorded at elevated temperatures were obtained using a Specac high temperature cell mounted in the spectrometer and Micristar heat controller. This device has a reported accuracy of ±0.1°C. Details of the preparation of samples for *FT*i.r. analysis have been described previously[1]. Films used in this study were sufficiently thin to be within an absorbance range where the Beer–Lambert law is obeyed (<0.6 absorbance units). Thermal analysis was performed on a Perkin–Elmer 7 Series differential scanning calorimeter. A heating rate of $20°\mathrm{C\,min}^{-1}$ was employed using a sample size of *ca.* 10–15 mg.

RESULTS AND DISCUSSION

In marked contrast to the previously described APU–EPO blend system[1], experimental infra-red and thermal analysis results unambiguously demonstrate that the APU–PVME blend system is immiscible at 110°C. The carbonyl stretching region of the infra-red spectra of samples of APU–PVME blends is indistinguishable from that of the pure APU at the same temperature; a reflection of the absence of urethane–ether interactions and the lack of significant molecular mixing (*Figure 1*). In addition, two distinct T_g values in the proximity of the pure components were observed over the entire composition range, as illustrated in *Figure 2*. As mentioned earlier, these were unexpected results. PVME is miscible with a large number of different polymers, including polystyrene[6], PVPh[7], the poly(hydroxy ether of bisphenol A) (Phenoxy)[8] and several poly(ethylene-*co*-methacrylic acid)s[9]. In common with EPO, PVME contains an ether oxygen capable of forming a hydrogen bond with labile protons and it is anticipated that there are only small differences in the relative strengths of the

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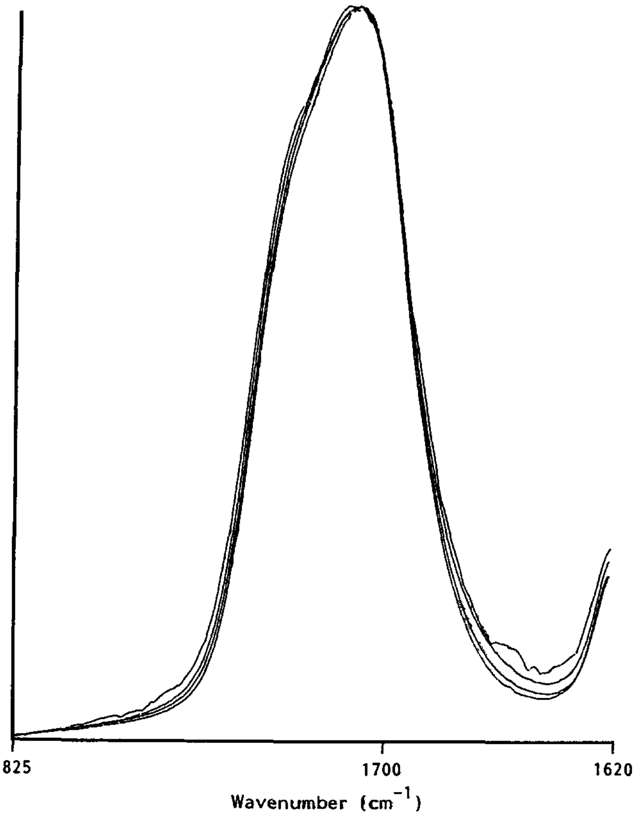

Figure 1 Carbonyl stretching region of the infra-red spectra of APU–PVME mixtures containing 20, 50, 80 and 100 wt% APU and recorded at 110°C

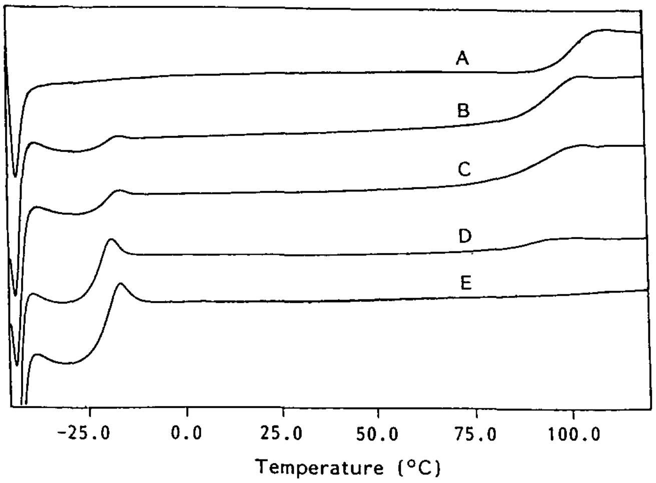

Figure 2 D.s.c. thermograms of APU–PVME blends containing (A) 100, (B) 80, (C) 50, (D) 20 and (E) 0 wt% APU

interactions between the urethane N–H group and these two different ether oxygens.

On the other hand, infra-red spectroscopic and thermal analyses indicate that APU–PEO blends are miscible at 110°C. Representative spectra in the carbonyl stretching region (1640–1800 cm^{-1}) of APU–PEO blend samples recorded at 110°C, above the melting point of PEO, are shown in *Figure 3*. The pure APU is characterized by a major band centred at approximately 1710–1715 cm^{-1}, ascribed to hydrogen-bonded urethane C=O groups, and a shoulder at about 1735 cm^{-1} attributed to 'free' or non-hydrogen-bonded C=O groups[1]. With increasing amounts of PEO in the blend, the relative proportion of 'free' to hydrogen-bonded carbonyls also increases. This is consistent with the premise that when N–H groups interact with ether oxygens they liberate an equal number of 'free' C=O groups[1]. Studies using PEO polymers of molecular weights ranging from 100 000 to 5 000 000 suggest that the degree of mixing is not a strong function of molecular weight.

In essence, can we rationalize the fact that the amorphous polyurethane blends containing PEO and EPO are miscible while the corresponding blends with PVME are immiscible? In the past we probably would have been content to invoke steric hindrance or minor differences in the enthalpy and entropy of the 'different' urethane–ether interactions to explain such apparent anomalies. Now, however, we can test the sensitivity of the recently formulated theory[3,4] and calculate the free energy of mixing and the spinodal curves for such systems to see if such behaviour is predicted. There are a number of parameters required and a few important assumptions to be made, however, before we can calculate the free energy of mixing and the theoretical phase diagrams.

Stoichiometry and the estimation of equilibrium constants

A quantitative infra-red analysis of the fraction of 'free' C=O groups present in APU–EPO blends of varying composition at 110°C has been described in detail previously (see Table 2 in ref. 1) and will not be repeated here. For pure APU, the fraction of 'free' C=O groups was determined to be 0.163. This corresponds to a value of the equilibrium constant describing the self-association

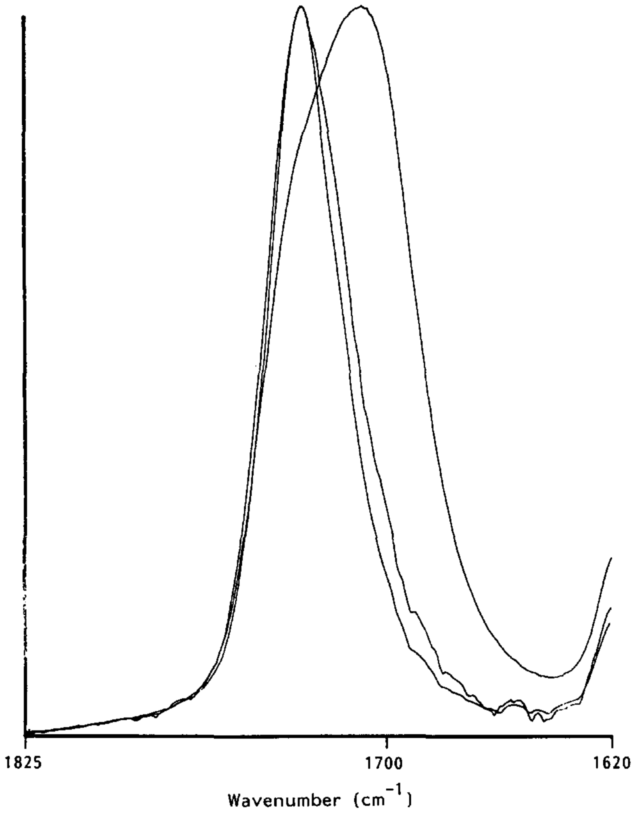

Figure 3 Carbonyl stretching region, recorded at 110°C, of the infra-red spectra of pure APU and two 20:80 wt% APU–PEO mixtures containing PEO polymers of different molecular weights (100 and 5000K)

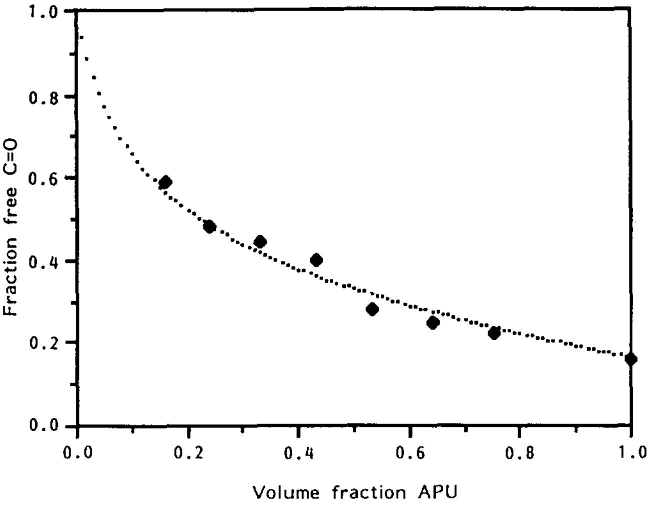

Figure 4 Comparison of the (◆) experimentally and (■) theoretically ($K_B = 31.5$, $K_A = 1.47$) determined fraction of 'free' or non-hydrogen-bonded urethane carbonyl groups as a function of the volume fraction of APU

of APU at 110°C of $K_B = 31.5$ (equation XXXVIII in ref. 2).

In a similar manner, the value of the equilibrium constant describing the association of urethane and ether units K_A was also determined directly from infra-red measurements[1]. The stoichiometry of such systems is described by the two equations[3]:

$$\Phi_B = \frac{\Phi_{B_1}}{(1 - K_B\Phi_{B_1})^2}\left(1 + \frac{K_A\Phi_{0A}}{r}\right) \tag{1}$$

$$\Phi_A = \Phi_{0A}\left[1 + \frac{K_A\Phi_{B_1}}{(1 - K_B\Phi_{B_1})}\right] \tag{2}$$

where Φ_A and Φ_B are the volume fractions of non-self-associating species A and self-associating species B, respectively, Φ_{0A} and Φ_{B_1} are the volume fractions of the respective totally 'free monomers', and r is the ratio of the molar volumes of the repeat units, V_A/V_B. Note that here the subscripts refer to the *chemical repeat units*, not the 'interacting' unit. These equations describe the stoichiometry of associating species and are equally valid when expressed in terms of 'interacting units' or chemical repeat units[3].

Figure 4 shows the experimental values of the fraction of 'free' (non-hydrogen-bonded) urethane carbonyl groups as a function of the volume fraction of APU in blends of this polymer with EPO. Employing the value for K_B at 110°C determined above (31.5) and selecting an initial value for K_A together with the appropriate value[1] of r (0.43), we calculated the roots (Φ_{B_1}) iteratively using Newton's method for given values of Φ_B over the whole composition range (eq. (1) and (2)). The fraction of 'free' urethane groups[2] as a function of the volume fraction of APU is then simply given by $[1 - K_B\Phi_{B_1}]$. The value of K_A was systematically varied and a least squares method employed to determine the best fit of the experimental data for the APU blends with EPO. The theoretical curve derived from the best estimate of $K_A = 1.47$ is also illustrated in *Figure 4*. The splendid fit is most encouraging. All things being equal (i.e. no major changes in chemistry, steric hindrance etc.), we theoretically[3] expect to find identical values of K_A for similar APU–polyether blends. The difference in the size of the chemical repeat units is accounted for by the factor K_A/r in the equations.

Calculation of the free energy of mixing

Having obtained the two equilibrium constants, K_B and K_A, we are now in a position to calculate the free energy of mixing using the equations we have recently derived (ref. 3 contains a detailed description of all the parameters involved). In summary, the relevant equations are:

$$\frac{\Delta G^M}{RT} = \frac{\Phi_A}{N_A}\ln\Phi_A + \frac{\Phi_B}{N_B}\ln\Phi_B + \Phi_A\Phi_B\chi + \frac{\Delta G_H}{RT} \tag{3}$$

where

$$\frac{\Delta G_H}{RT} = \frac{1}{s_B}\left[\begin{array}{l}\left[\Phi_B\ln\left\{\dfrac{\Phi_{B_1}}{\Phi^0_{B_1}}\cdot\left(\dfrac{1}{\Phi_B}\right)^{1/\bar{n}^0_H}\right\} + \dfrac{\Phi_A}{r}\ln\left\{\dfrac{\Phi_{0A}}{\Phi_A}\right\}\right] \\ + \Phi_B K_B\left(\Phi_{B_1} - \Phi^0_{B_1}\right) + \Phi_B(1 - K_B\Phi_{B_1})\left\{\dfrac{\dfrac{K_A\Phi_{0A}}{r}}{1 + \dfrac{K_A\Phi_{0A}}{r}}\right\}\end{array}\right] \tag{4}$$

The superscript 0 denotes the parameter in the pure state and:

$$\bar{n}^0_H = \left[\frac{1}{1 - K_B\Phi^0_{B_1}}\right] \tag{5}$$

Before calculating the free energy of mixing, values for the molar volumes and degrees of polymerization of A and B, the interaction parameter χ, and the number of segments in the APU chemical repeat unit, s_B, are needed. We now consider the source and justification of the values employed for these parameters. The molar volumes of the chemical repeat units of APU, EPO, PEO and PVME were calculated from the individual group contributions listed by van Krevelen[10] to be 108.3, 46.3, 41.4 and 57.6 $cm^3\,mol^{-1}$, respectively. The number of segments in a chemical repeat unit of the self-associating component[3], s_B, was estimated from the molar volume of the APU repeat unit relative to that of the urethane group to have a value of 3.1. The degree of polymerization for all the polymers was assumed to be $N_A = N_B = 250$.

The interaction parameter, χ, which in the theory represents a non-hydrogen-bonding contribution to the free energy of mixing, is estimated from the solubility parameters of the two polymers using the molar attraction constants approach of Hoy[11]. An effective non-hydrogen-bonded solubility parameter of APU is determined from a structure, identical to that of APU, but without the active N–H proton (i.e. the molar attraction constants for the urethane group are substituted by those of a tertiary amine and an ester). Solubility parameters of 9.72, 8.83, 9.13 and 8.33 $(cal\cdot cm^3)^{0.5}\,mol^{-1}$ were determined for APU, EPO, PEO and PVME, respectively. This leads to estimates of the value of χ of 0.145, 0.064 and 0.353 for physical interactions between APU and EPO, PEO and PVME, respectively[12], using the molar volume of the APU repeat as the reference volume, V_r.

Employing the parameters described above in equations (1)–(5), the free energy of mixing was calculated

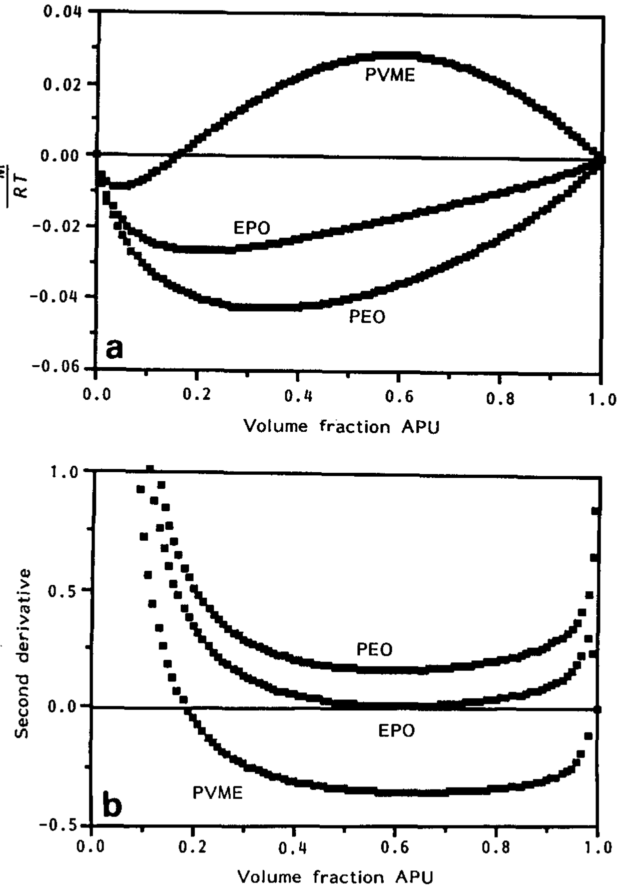

Figure 5 (a) Calculated free energy of mixing and (b) second derivatives of the free energy for APU–polyether blends at 110°C

at 110°C as a function of the volume fraction of APU in blends with PEO, EPO and PVME. The results are displayed in *Figure 5*, which also includes the second derivative of the free energy with respect to APU volume fraction. The calculated results predict that at 110°C the APU blends with PEO are miscible. The free energy of mixing is negative and the second derivative is positive throughout the whole composition range. At the other extreme, the APU–PVME blend system is predicted to be immiscible. The free energy is not negative throughout the entire composition range and the second derivative assumes negative values over a wide composition range. It is interesting to note that our calculations predict that APU blends with EPO are miscible but not far from instability—the second derivative curve is very close to assuming negative values.

The spinodal may be readily determined by equating the second derivative to zero while the binodal was calculated by searching for equivalent chemical potentials outside the spinodal consistent with a common tangent to the free energy curve. But for this we need to calculate the free energy as a function of temperature, which in turn requires us to make two further assumptions. A simple van't Hoff temperature dependence of the equilibrium constants K_B and K_A is assumed, implying a constant ΔH over the entire temperature range considered (-150 to 500°C). Identical values ($-5.0\,\mathrm{kcal\,mol^{-1}}$) for the enthalpy of hydrogen bond formation, corresponding to both equilibrium constants K_B and K_A, were also assumed[1]. Finally, the temperature dependence of the interaction parameter, χ, is assumed to follow a simple inverse temperature relationship in this study.

Calculation of the phase diagrams

The results of the calculations are shown in *Figures 6–8*. The phase diagram of the APU–PEO system (*Figure 6*) shows a theoretical 'window of miscibility' across the entire composition range up to about 270°C (unfortunately much above the degradation temperature). At the other extreme, the phase diagram of APU–PVME (*Figure 8*) shows the classic 'hour glass' shape typical of an immiscible system. It should perhaps be emphasized that modest changes to the values of the parameters employed in the calculations will not significantly affect the general features of the phase diagrams illustrated in *Figures 6* and *8*. This is readily understood if one considers the overall balance of equation (3). In a case where both polymers have high molecular weights (combinatorial entropy terms are therefore negligible), then the free energy of mixing is determined by the balance between the $\Phi_A\Phi_B\chi$ and the hydrogen-bonding terms. If the latter should dominate, then a phase diagram of type shown in *Figure 6* will result. Conversely, a phase diagram of type shown in *Figure 8* will result should the $\Phi_A\Phi_B\chi$ term dominate.

Where it becomes very interesting is in the transition

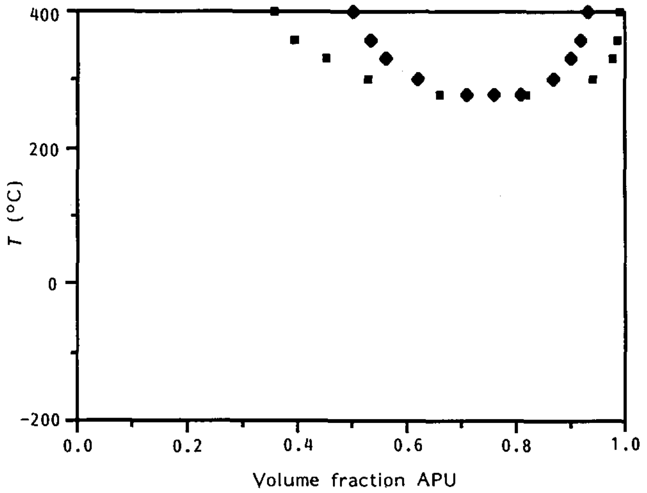

Figure 6 Calculated spinodal (◆) and binodal (■) for APU–PEO blends

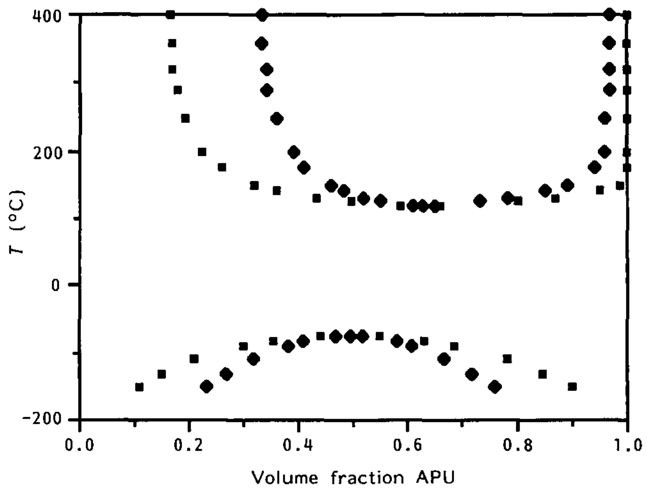

Figure 7 Calculated spinodal (◆) and binodal (■) for APU–EPO blends

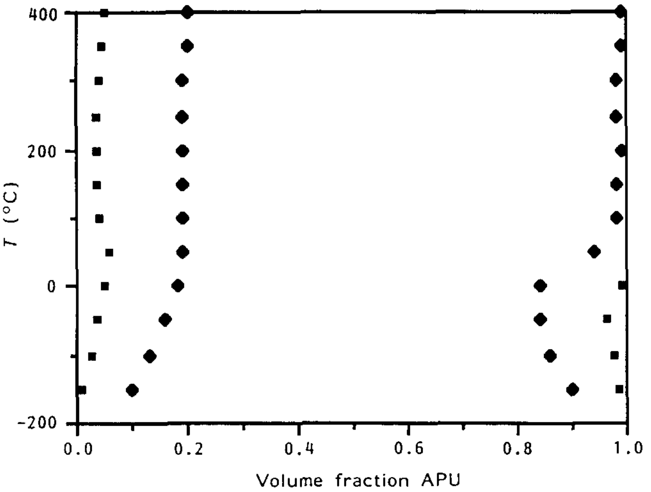

Figure 8 Calculated spinodal (◆) and binodal (■) for APU–PVME blends

between these two types of phase diagrams, when these two major contributors are roughly equivalent in magnitude. An excellent example is the phase diagram calculated for the APU–EPO blends (*Figure* 7). Our calculations indicate that there is a 'window of miscibility' occurring between about −50 and 120°C. Changes in molecular weight, equilibrium constants, interaction parameter, etc. can now dramatically alter the appearance of the phase diagram and affect the 'windows of miscibility'. Although we know that the APU–EPO system is miscible at 110°C, the disposition towards thermal degradation unfortunately precludes experimental verification of a lower critical solution temperature. Nonetheless, we are encouraged by the broad concurrence between the theoretical predictions and experimental results pertaining to the miscibility of APU–polyether blends.

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