Prediction of phase-separated regions in ternary blends composed of three miscible binary copolymer pairs

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The phase behaviour of ternary copolymer blends poly(styrene-*stat*-acrylonitrile) (SAN)/poly(methyl methacrylate-*stat*-acrylonitrile) (MAN)/poly(*N*-phenylitaconimide-*stat*-methyl methacrylate) (PIMMMA) was analysed using Flory–Huggins theory. The system studied consists of the combination of three binary pairs SAN/MAN, SAN/PIMMMA and MAN/PIMMMA, and it has been demonstrated that the combination of these three miscible pairings cannot guarantee the formation of a single-phase ternary blend. Phase-separated regions in ternary space can appear at compositions defined by the miscible windows of the binary pairings, provided that the difference in the interactions between them is large. When the molecular weights of the three polymers are unequal, it is suggested that a modified term $\Delta\chi' = (\chi'_{13} - \chi'_{12})$ is used to replace the normal $\Delta\chi$, in order to reflect the influence of molecular weight on the asymmetry of the interactions between the different binary polymer pairs. The new term $\chi'_{ij} = (\chi_{ijcrit} - \chi_{ij})$, where $\chi_{ijcrit} > \chi_{ij}$, is the difference between the critical interaction parameter and the corresponding normal interaction parameter of the *i–j* pair. It will equal the original expression for $\Delta\chi$ only when the component molecular weights are equal.

(Keywords: ternary blends; copolymer; Flory–Huggins theory)

INTRODUCTION

There are three binary pairs (1–2, 1–3 and 2–3) in a mixture consisting of three components (designated 1, 2 and 3) and a balance of the interactions between all three will determine the overall phase behaviour of the mixture. Scott[1] and Tompa[2] were the first to describe ternary systems involving two polymers and one solvent using the Flory–Huggins (FH) mean-field theory. They found that for the condition of equal polymer–solvent interactions, i.e. $\chi_{12} = \chi_{13}$, the phase behaviour of the mixture was controlled mainly by the value of χ_{23}, the polymer–polymer interaction. Zeman and Patterson[3] later demonstrated that phase separation in ternary systems is strongly promoted by any asymmetry in the polymer–solvent interactions ($\chi_{12} \neq \chi_{13}$), the so-called $\Delta\chi$ effect. Even if each of the binary pairs is miscible, in combination they may produce an immiscible ternary blend provided that the value of $\Delta\chi$ is sufficiently large. The corresponding spinodals defining the phase-separated regions are closed loops which do not touch the edges of the Gibbs triangular phase diagram. This has been observed experimentally by Robard and co-workers[4,5] in a mixture of chloroform/polystyrene/poly(vinyl methyl ether). If this principle is extended to ternary systems consisting of three polymers, it implies that three miscible polymers could form an immiscible ternary blend. However, until now little work on ternary polymer systems has been reported[6].

An extensive series of papers[6–11] dealing with the miscibility of binary polymer blends, in which at least one of the components is a statistical copolymer, has been published from this laboratory. The phase behaviour of such systems has been analysed on the basis that an overall interaction parameter for the blend may be expressed as a function of the constituent copolymer compositions[7,12]. For a general blend consisting of two statistical copolymers, A_xB_{1-x} and C_yD_{1-y}, where x and y are composition volume fractions, the expression for the blend interaction parameter is as follows:

$$\chi_{blend} = xy\chi_{AC} + y(1-x)\chi_{BC} + x(1-y)\chi_{AD} + (1-x)(1-y)\chi_{BD} - x(1-x)\chi_{AB} - y(1-y)\chi_{CD} \quad (1)$$

where χ_{ij} quantifies the interaction parameter between copolymer segments i and j.

In contrast to the situation in homopolymer blends, in which the interaction parameter for the blend is formally unalterable, equation (1) shows that interaction parameters for copolymer blends are functions of the copolymer compositions, and so it should be possible to produce some value of the blend interaction parameter χ_{blend} which will ensure single-phase behaviour, even though the corresponding homopolymers may not themselves be miscible[6–11]. Similarly, it may be possible to produce an immiscible ternary mixture from three miscible binary copolymer pairings, forming a closed

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loop in the corresponding phase diagram. The aim of the present paper is to demonstrate this experimentally.

The phase behaviour of ternary copolymer blends of poly(styrene-*stat*-acrylonitrile) (SAN, component 1)/poly(methyl methacrylate-*stat*-acrylonitrile) (MAN, component 2)/poly(*N*-phenylitaconimide-*stat*-methyl methacrylate) (PIMMMA, component 3) is studied here using FH theory. Of the three binary blends, SAN/MAN (1–2), SAN/PIMMMA (1–3) and MAN/PIMMMA (2–3), the first two (1–2 and 1–3) are miscible based on previous work[8–11] while the third (2–3) is found to be miscible only in certain composition regions and at relatively low molecular weights of the components. The necessary segmental interaction parameters have been estimated previously[10,11] to be $\chi_{SMMA}=0.03$, $\chi_{SAN}=0.83$, $\chi_{SPIM}=0.16$, $\chi_{MAN}=0.32$ (for intermolecular pairing), $\chi_{MAN}=0.46$ (for intramolecular pairing) and $\chi_{PIMMMA}=0.047$. From these, the binary interaction parameters (χ_{ij}; $i,j=1,2,3$) which describe the ternary mixtures can be evaluated from equation (1). The strategy employed to calculate ternary spinodal and binodal boundaries is similar to that reported elsewhere[11].

It should be pointed out that the original application of the FH theory to describe the $\Delta\chi$ effect[3] is based on the precondition that the molecular weights of the components are equal, and this needs to be modified if they are unequal and not infinite. A discussion on this is given in relevant sections of the paper.

EXPERIMENTAL

The synthesis of *N*-phenylitaconimide (PIM) is the same as described previously[9]. Other monomers, styrene (S), methyl methacrylate (MMA) and acrylonitrile (AN), were freed from inhibitor and distilled prior to use. The statistical copolymers of SAN and MAN were synthesized by conventional free radical solution copolymerization at ca. 338 K, with toluene as solvent and α, α′-azobisisobutyronitrile (AIBN) as initiator. Copolymers of PIMMMA were synthesized at 338 K in tetrahydrofuran (THF) solution, also using AIBN as initiator.

Copolymer compositions were determined by CHN elemental analysis and expressed in volume fractions using the molar volumes of the copolymer repeat units. The molecular weights were measured by gel permeation chromatography with polystyrene as the calibration standard. The degree of polymerization is based on the number average of the copolymer molecular weights. The characterization details for the samples used are shown in *Table 1*.

Copolymer blends were prepared by codissolution of the three components in THF followed by coprecipitation into methanol. The powder samples were then vacuum dried at 333 K for 48 h. The glass transition temperatures (T_g) of all copolymer samples and of their blends were determined using a Perkin–Elmer DSC-4 differential scanning calorimeter at a heating rate of 20 K min^{-1}. Blend miscibility was judged using the criterion that a miscible blend exhibits a single T_g whereas an immiscible blend shows multiple T_gs corresponding to the glass transitions of the components.

Table 1 Composition, molecular weight and distribution, and glass transition temperatures of statistical copolymers SAN, MAN and PIMMMA

Copolymer composition	M_n (g mol^{-1})	M_w/M_n	T_g (K)
SAN 1 (63.0 vol% S)	52 400	1.80	382
SAN 2 (70.0 vol% S)	51 700	1.80	382
MAN 1 (68.0 vol% MMA)	24 200	1.60	347
MAN 2 (95.0 vol% MMA)	37 000	1.60	363
PIMMMA 1 (88.0 vol% PIM)	11 000	1.70	486
PIMMMA 2 (55.0 vol% PIM)	43 200	1.70	423

RESULTS AND DISCUSSION

If the molecular weights of the components in a ternary blend composed of three miscible binary blends are equal, or approximately so, the conditions for the appearance of an unstable region in the system are (i) each $\chi_{ij} \leqslant \chi_{ijcrit}$ (miscible binary blends) and (ii) the value $\Delta\chi$ is large. The corresponding spinodals are then closed loops. *Figure 1* shows that, for the MAN/PIMMMA pair to meet this requirement (i.e. $\chi_{23} \leqslant \chi_{23crit}$ with $\chi_{23crit}=0$) the PIM content in PIMMMA should be greater than ca. 95 vol%, although this restriction could be reduced to about 85–90 vol% if the corresponding component molecular weights decrease accordingly. In the light of this limitation the other two binary interaction parameters, χ_{12} for SAN/MAN and χ_{13} for SAN/PIMMMA, were calculated as a function of the volume fraction of S in SAN and are shown for different MMA volume fractions in MAN in *Figure 2*. Miscible 'windows' for the SAN/MAN 1–2 pair are predicted when S in SAN is between about 40 and 70 vol% and when MMA in MAN is between about 65 to 75 vol%. Also shown in *Figure 2* is the much wider window for the 1–3 pair (SAN/PIMMMA) where the PIM is 90 vol%. Multiphase regions for ternary blends should lie within these composition ranges defined by the binary systems.

A binary SAN/MAN mixture with 65 vol% MMA and 65 vol% S is immiscible (represented by the filled circle in *Figure 2*) and so the spinodal intersects the 1–2 edge of the ternary phase diagram as shown in *Figure 3*. If S

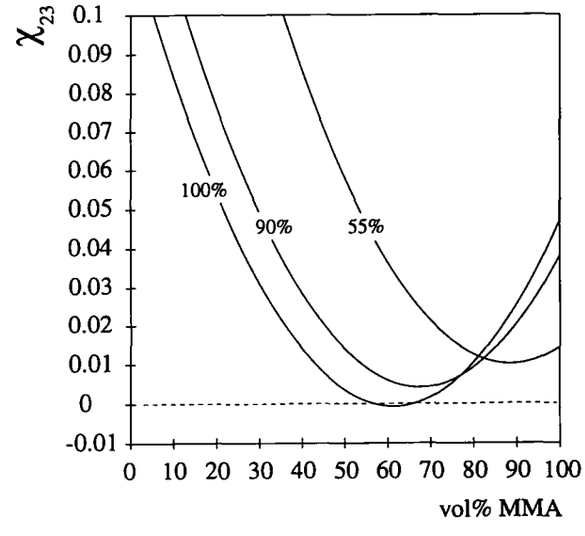

Figure 1 Calculated χ_{23} curves for MAN/PIMMMA blends for various vol% PIM in PIMMMA (component 3) plotted against the MMA composition in MAN (component 2)

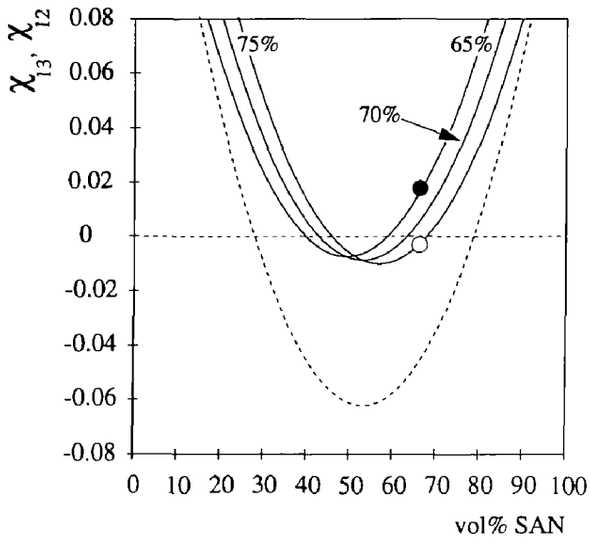

Figure 2 Calculated χ_{12} and χ_{13} curves plotted as a function of the vol% S in SAN (component 1). Full lines are χ_{12} for the indicated compositions of MMA in MAN (component 2). Dashed line is χ_{13} for 90 vol% PIM in PIMMMA (component 3)

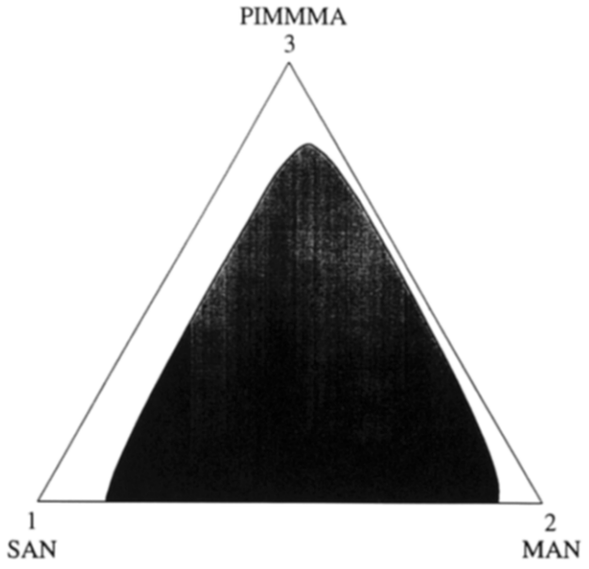

Figure 3 Calculated spinodal boundary for the ternary blend SAN (S 65 vol%)/MAN (MMA 65 vol%)/PIMMMA (PIM 90 vol%); $\chi_{12}=0.0127$, $\chi_{13}=-0.0436$, $\chi_{23}=0.00437$, $N_1=521$, $N_2=310$, $N_3=56$

is now 65 vol% and MMA is 75 vol% (a miscible combination indicated by the open circle in *Figure 2*) immiscible ternary mixtures with PIMMMA will be formed due to the large difference between χ_{12} and χ_{13}, and consequently a spinodal closed loop appears in the calculated ternary diagram shown in *Figure 4*. The extent of this ternary unstable region may be predicted from the symmetry of the χ_{12} and χ_{13} curves in *Figure 2*, which guarantees a large $\Delta\chi$ effect. For example, closed loops appear in the range of S content of 45–65 vol% (when the MMA is around 70 vol%) as exemplified in *Figure 5*.

As noted earlier, the original theory underlying the $\Delta\chi$ effect has the precondition that the component molecular weights are equal. This must be modified in order to reflect the considerable influence of chain length in systems with unequal molecular weights. It can be seen from *Figures 6* and *7* that the spinodal shapes vary strongly with changes in the degree of polymerization (N_i) of the components, while the $\Delta\chi$ values for the systems are held constant.

In any binary system, miscibility is judged by the criterion $\chi_{ij} \leqslant \chi_{ijcrit}$, where

$$\chi_{ijcrit} = 0.5(N_i^{-1/2} + N_j^{-1/2})^2 \qquad (2)$$

and N_i and N_j are the degrees of polymerization of components i and j (here $i=1$, $j=2$). This is the unique criterion which dictates the phase behaviour of the mixture, but in a ternary system the interactions between components 1 and 2 will be influenced by the third

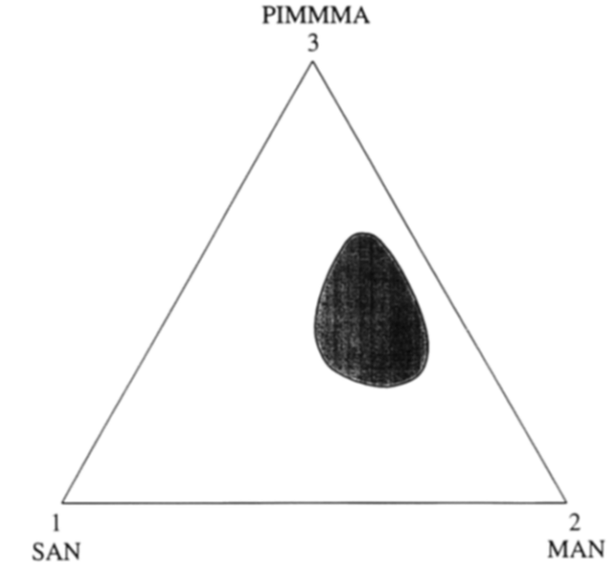

Figure 4 Calculated spinodal boundary for the ternary blend SAN (S 65 vol%)/MAN (MMA 75 vol%)/PIMMMA (PIM 90 vol%); $\chi_{12}=-0.00470$, $\chi_{13}=-0.0436$, $\chi_{23}=0.00600$, $N_1=521$, $N_2=310$, $N_3=56$

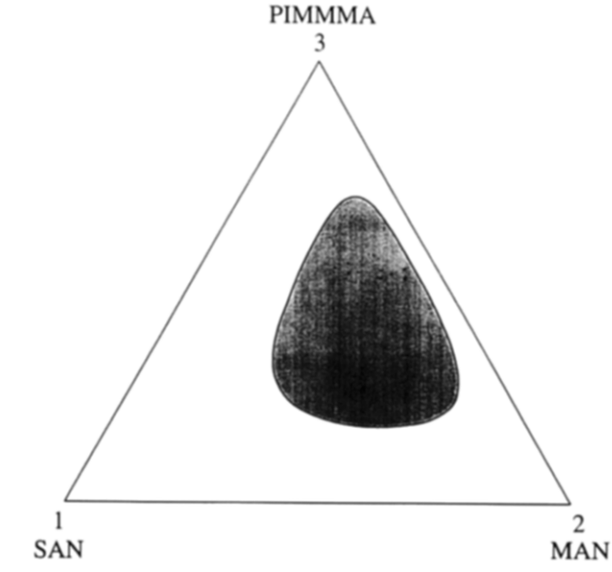

Figure 5 Calculated spinodal boundary for the ternary blend SAN (S 60 vol%)/MAN (MMA 70 vol%)/PIMMMA (PIM 90 vol%) with $\Delta\chi=0.0488$ and $\Delta\chi'=0.0594$; $\chi_{12}=-0.00487$, $\chi_{13}=-0.0536$, $\chi_{23}=0.00438$, $N_1=521$, $N_2=310$, $N_3=56$

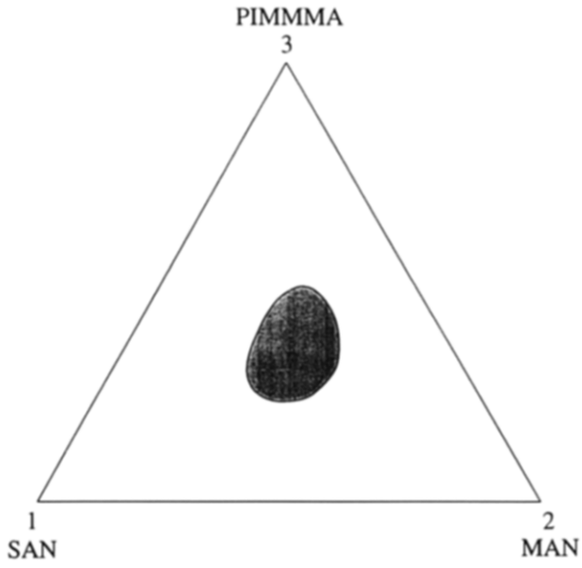

Figure 6 Calculated spinodal boundary for the ternary blend SAN (S 63 vol%)/MAN (MMA 68 vol%)/PIMMMA (PIM 88 vol%) with $\Delta\chi = 0.0507$ and $\Delta\chi' = 0.0567$; $\chi_{12} = 0.00266$, $\chi_{13} = -0.0480$, $\chi_{23} = 0.00470$, $N_1 = 100$, $N_2 = 310$, $N_3 = 56$

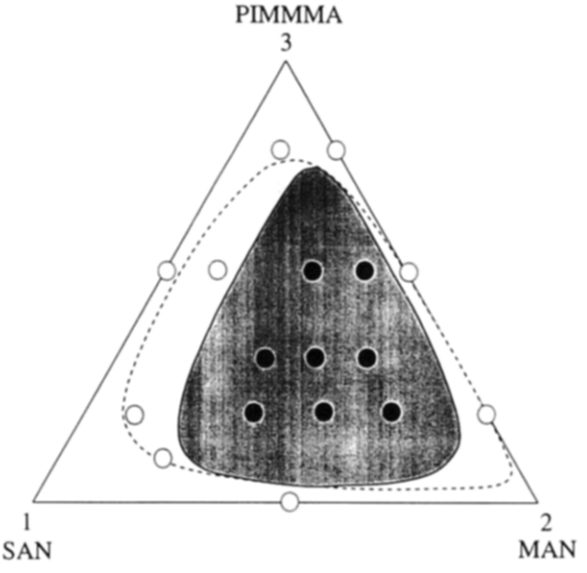

Figure 7 Calculated spinodal and binodal boundaries for ternary blend SAN (S 63 vol%)/MAN (MMA 68 vol%)/PIMMMA (PIM 88 vol%) with $\Delta\chi = 0.0507$ and $\Delta\chi' = 0.0614$; $\chi_{12} = 0.00260$, $\chi_{13} = -0.0480$, $\chi_{23} = 0.00470$, $N_1 = 521$, $N_2 = 310$, $N_3 = 56$. Spinodal (full line) encloses darker shaded (unstable) region; binodal (dashed line) encloses lighter shaded (metastable) region. Experimental points: ○, miscible blend; ●, immiscible blend

component, which has the opportunity to interact with either components 1 or 2. Component 3 may actually compete with 1 (or 2) for component 2 (or 1) according to their interaction energies. This competition may be quantified by the difference between the critical and the binary interaction parameter for each pair, i.e. the value of $\chi'_{ij} = \chi_{ijcrit} - \chi_{ij}$. The overall phase behaviour will then depend on the net effect of these competitive interactions. If the molecular weights of the polymers are different, the χ_{ijcrit} of each i–j binary pairing will be unequal. A modified term $\Delta\chi'$ is suggested as a measure of any asymmetry between the competitive binary interactions. Since χ'_{12} represents the difference between χ_{12crit} and χ_{12} for the 1–2 pair and correspondingly χ'_{13} for the 1–3 pair, the original $\Delta\chi$ effect can be rewritten as follows:

$$\begin{aligned}\Delta\chi' &= \chi'_{13} - \chi'_{12} \\ &= (\chi_{13crit} - \chi_{13}) - (\chi_{12crit} - \chi_{12}) \\ &= \chi_{13crit} - \chi_{12crit} + \chi_{12} - \chi_{13} \\ &= \Delta\chi_{crit} + \Delta\chi \end{aligned} \quad (3)$$

For the condition of equal molecular weights $\Delta\chi_{crit}$ is zero and $\Delta\chi' = \Delta\chi$. In a ternary system, if the interaction parameter χ_{13} is the smallest and χ_{12} is set less favourable, as is the case in *Figures 5* and *6*, then any variations of polymer molecular weight which would lead to an increase of χ'_{13} and a decrease of χ'_{12} (i.e. enhancing $\Delta\chi'$) will intensify the asymmetry of the two competitive interactions between the 1–3 and the 1–2 pair, thereby promoting phase separation. The opposite effect occurs if the changes in molecular weight cause $\Delta\chi'$ to decrease. For example, the extensive two-phase region in *Figure 7*, obtained from the values of the parameters shown in the legend, collapses to give complete miscibility at all compositions when N_1, N_2 and N_3 are reordered as 521, 56 and 310, respectively, to give $\Delta\chi' = 0.04$.

These phase diagrams, calculated from FH theory, conform satisfactorily to the experimental data available, as shown in *Figures 7* and *8*. The more accurate estimate of the experimental boundaries between miscible and immiscible regions is obtained from the spinodal condition. This result was observed and reported previously[11] for the ternary system SAN/MAN/SMMA. *Figure 7* also demonstrates experimentally that mixing three miscible binary blends does not guarantee a miscible ternary blend. By choosing the appropriate compositions and molecular weights of each constituent copolymer it is possible to form an immiscible ternary blend from three pairwise miscible components.

The corresponding d.s.c. measurements show that there are two T_gs, appearing at about 433 and 363 K, if the SAN fraction in the ternary mixture is below about 60 vol%, indicating the existence of at least two phases in the mixture. The former T_g position is quite close to that of the most energetically favourable binary pair SAN/PIMMMA, whereas the latter is near to both T_g values for the other two binaries SAN/MAN (368 K) and MAN/PIMMMA (364 K). This makes it difficult to estimate what the composition of that phase might be, but some understanding of the phase structures may be possible from an analysis of the χ_{ij} values for each binary pair. It is known from the three χ_{ij} values that the 1–3 pair (SAN/PIMMMA) is energetically the most favourable, and mixing SAN into the binary mixture MAN/PIMMMA should weaken or break the contacts between MAN and PIMMMA, thus promoting phase separation. If this is indeed the case, the final phase of the blend should consist of two domains, one composed mainly of the most favourable binary pair, MAN/PIMMMA, and the other containing mostly MAN with some residual SAN and/or PIMMMA. When the SAN concentration is high (e.g. over 70 vol%), a single homogeneous phase is possible (as in *Figure 7*). This might be attributed to

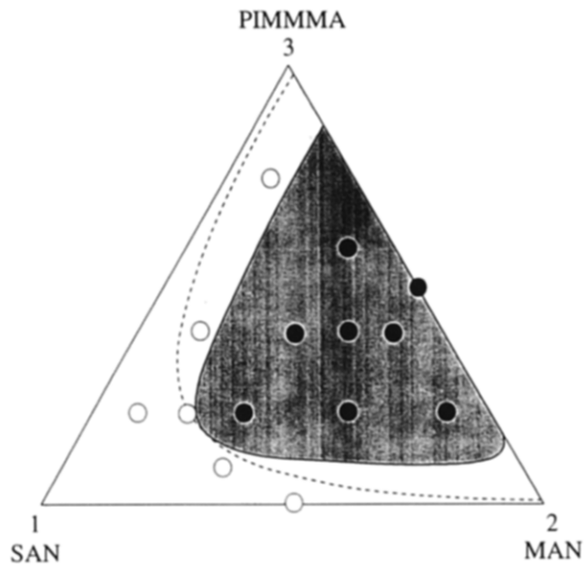

Figure 8 Calculated spinodal and binodal boundaries for ternary blend San (S 70 vol%)/MAN (MMA 95 vol%)/PIMMMA (PIM 55 vol%); $\chi_{12} = -0.0156$, $\chi_{13} = -0.0317$, $\chi_{23} = 0.0115$, $N_1 = 650$, $N_2 = 386$, $N_3 = 320$. Spinodal (full line) encloses darker shaded (unstable) region; binodal (dashed line) encloses lighter shaded (metastable) region. Experimental points: ○, miscible blend; ●, immiscible blend

the formation of a continuous SAN phase in the mixture bridging the two less miscible components, MAN and PIMMMA. Further work is required to determine fully the multiphase structures and compositions in ternary systems.

Finally, it should be mentioned that miscibility in these complex systems could be influenced by the sequence distributions in the copolymers[12-17], but this would be difficult to determine and assess. While we have no direct measurement of the sequence distribution in our samples, the interaction parameters estimated from experimental data are likely to contain any contributions from this effect which, though hidden, would be subsumed in the calculated value of χ_{ij}.

CONCLUSIONS

The phase behaviour of ternary copolymer blends SAN/MAN/PIMMMA has been examined using Flory–Huggins theory. By taking advantage of copolymer blends whose interaction parameters can be varied by controlling the copolymer compositions, it has been demonstrated that the combination of three miscible binary (co)polymer blends does not guarantee miscible ternary blends. An unstable region may lie within the composition regions defined by the miscible windows of the binary systems, provided that the differences in the interactions between these binary pairs are sufficiently large. When the component molecular weights are unequal, a modified term $\Delta\chi'$ is suggested as an appropriate replacement for the $\Delta\chi$ effect, which is normally used as a measure of the asymmetry of interactions between two binary pairs.

This interesting behaviour has also been found in other ternary polymer blends studied in this laboratory, and further work is in progress to determine whether or not it is a general phenomenon of ternary systems containing copolymers.

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