Miscibility of blends of α-methyl styrene/acrylonitrile copolymers with styrenic copolymers containing acrylonitrile or maleic anhydride

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Blends of α-methyl styrene/acrylonitrile copolymers with styrene/acrylonitrile copolymers and with styrene/maleic anhydride copolymers are shown to exhibit regions of miscibility that appear to depend rather sensitively on component molecular weights. These blends did not exhibit lower or upper critical solution temperature phase behaviour. A refined set of monomer unit pair interaction energies are given that reasonably describe the experimental results in terms of the Flory–Huggins theory.

(Keywords: blends; acrylonitrile copolymers; maleic anhydride copolymers)

Introduction

The phase behaviour of blends of styrene/acrylonitrile (SAN) copolymers with various homopolymers and copolymers has been studied extensively [1–19]. The structurally related copolymers of α-methyl styrene and acrylonitrile (α-MSAN) also form miscible blends with various homopolymers[18,20–26]. However, it has been found that substituting α-methyl styrene (α-MS) for styrene in these copolymers greatly influences the phase behaviour of some blends. Analysis of the miscibility boundaries has enabled determination of the Flory–Huggins binary interaction energies, B_{ij}, for the various monomer unit pairs involved.

The objective of this communication is to examine the regions of miscibility for blends of α-MSAN copolymers with SAN copolymers and with styrene/maleic anhydride (SMA) copolymers in terms of the binary interaction energies that govern the state of mixing of these blend systems. It has been shown[27,28] that polystyrene (PS) forms miscible blends with poly(α-methyl styrene) (P(α-MS)) when the molecular weights of both components are less than ~80 000. This might lead one to believe that blends of SAN copolymers with α-MSAN copolymers (i.e. AN is a common unit in both copolymers) would be miscible over a very broad composition range. However, Cowie *et al.*[29] reported that blends of these two copolymers have only a limited range of miscibility and deduced the applicable interaction energies from the observed copolymer–copolymer miscibility region. These authors suggested that it was necessary to distinguish between inter- and intra-segmental interaction energies to explain these observations. This study attempts to describe the miscibility behaviour of these blends using previously estimated binary pair interaction energies extracted from other polymer blend systems, where possible, without resort to this *ad hoc* distinction in interactions. Particular attention is drawn to the effect that component molecular weight has on miscibility of these blends.

Previous studies have shown that blends of SMA copolymers with SAN copolymers are miscible when the MA and AN comonomer contents are not too different, indicating that there is an exothermic interaction between the MA and AN comonomer[10,30–32]. Here, we explore the miscibility range for blends with SMA copolymers when the styrene in the SAN copolymer is replaced with α-MS.

Materials and procedure

Information on molecular weight and chemical composition for the α-MSAN, SAN and SMA copolymers used here has been given elsewhere[18,19,33] and is summarized in *Tables 1* and *2*. Blends were prepared by hot casting at 60°C from tetrahydrofuran (THF) in a Petri dish. Most of the blends were examined at 50/50 wt% ratio; however, in some cases, compositions ranging from 20 to 80 wt% were examined. Blends containing α-MSAN copolymers, where the AN content is 41 wt% and higher, or SAN copolymers, where AN content is 58.8 wt% and higher, were hot cast from dimethylformamide (DMF) or acetonitrile, since copolymers with such high AN contents do not dissolve in THF. The cast films were then dried at 60°C for 10 min in an air circulating oven until most of the solvent had evaporated. The resulting films were further dried in a vacuum oven at about 150°C for 2 days for blends where THF or acetonitrile was used as a solvent, and for 4 days for blends hot cast from DMF. The weight of the cast films was compared to the original polymer weight to make sure that all solvent was removed.

Glass transition temperatures (T_gs) were measured by a Perkin–Elmer DSC-7 at a heating rate of 20°C min^{-1}, using the onset method. The blends were examined for phase separation upon heating, lower critical solution

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Table 1 Values of B_{crit} (cal cm^{-3}) calculated from equation (3) for each pair of α-MSAN and SAN copolymers used for form blends in this study

	wt% α-MS in α-MSAN ($\bar{M}_w$)										
wt% S in SAN ($\bar{M}_w$)	42.4 (116 000)	51.5 (107 000)	58.6 (128 000)	70 (160 000)	76.6 (179 000)	80.6 (90 400)	83.6 (65 300)	88.1 (40 500)	90.6 (28 700)	93.5 (22 300)	100 (55 000)
31.0 (60 000)	0.024	0.025	0.023	0.021	0.021	0.027	0.031	0.040	0.048	0.056	–
37.4 (55 900)	0.025	0.026	0.024	0.022	0.021	0.028	–	–	–	–	–
41.2 (50 200)	0.027	0.028	0.026	0.024	0.023	0.029	–	–	–	–	–
60.0 (122 000)	0.018	0.017	0.015	0.018	0.021	0.022	0.024	0.029	0.035	0.040	–
67.7 (146 000)	0.015	0.016	0.014	0.017	0.018	0.020	0.021	0.027	0.032	0.034	–
75.0 (152 000)	0.015	0.015	0.014	0.014	0.016	0.019	0.021	0.027	0.029	0.031	–
84.5 (197 000)	–	–	0.013	0.013	0.014	0.015	0.016	0.020	0.025	0.027	–
91.0 (196 000)	–	–	0.013	0.012	0.012	0.015	0.016	0.017	0.022	0.024	0.020
100.0 (330 000)	–	–	–	0.011	0.008	0.012	0.015	0.016	0.016	0.016	0.018

Table 2 Values of B_{crit} (cal cm^{-3}) calculated from equation (3) for each pair of α-MSAN and SMA copolymers used to form blends in this study

	wt% AN in α-MSAN ($\bar{M}_w$)										
wt% S in SMA ($\bar{M}_w$)	0.0 (55 000)	6.5 (22 300)	9.4 (28 700)	11.9 (40 500)	16.5 (65 300)	19.4 (90 400)	23.4 (179 000)	30.0 (160 000)	41.4 (128 000)	48.5 (107 000)	57.6 (116 000)
0.0 (330 000)	0.018	0.034	0.027	0.021	0.015	0.012	0.008	0.009	–	–	–
2.0 (319 500)	–	–	0.028	0.022	0.015	–	–	0.009	–	–	–
8.0 (200 000)	–	0.038	0.032	0.025	0.018	0.015	0.010	0.011	0.013	–	–
14.0 (180 000)	–	0.039	0.033	0.026	0.019	0.016	0.011	0.012	0.013	0.014	0.014
18.1 (260 000)	–	0.036	0.029	0.023	0.017	0.014	0.009	0.009	0.011	0.012	0.012
25.0 (252 000)	–	0.036	0.030	0.024	0.017	0.014	0.009	0.010	0.011	0.013	0.012
33.0 (260 000)	–	0.036	0.030	0.024	0.017	0.014	0.009	0.010	0.011	0.013	0.012
48.5 (278 000)	–	0.036	0.030	0.024	0.017	0.014	0.009	0.010	0.011	0.013	0.012

temperature (*LCST*) behaviour and, on cooling, upper critical solution temperature (*UCST*) behaviour, either by visual observations or by use of a d.s.c. technique as described previously[17,34].

Experimental phase behaviour

Figure 1 shows the miscibility map for blends of α-MSAN copolymers with SAN copolymers. Miscible blends are indicated by open symbols while closed symbols denote immiscible blends. This classification was based on observations of optical clarity and glass transition behaviour. Blends of PS ($\bar{M}_w = 330\,000$) and P(α-MS) ($\bar{M}_w = 55\,000$) were cloudy and showed two T_gs by d.s.c., indicating immiscibility. This observation is supported by an extensive study of PS/P(α-MS) blends of varying molecular weights[35]. The experimental miscibility region shown in *Figure 1* is similar to that reported by Cowie *et al.*[29]. The miscible blends did not phase separate on heating prior to thermal degradation and the immiscible blends did not show any evidence of *UCST*-type phase behaviour. The state of miscibility observed for each copolymer pair was independent of composition within the range examined.

Figure 2 shows the region of miscibility for blends of α-MSAN copolymers with SMA copolymers as judged by T_g and blend clarity. Again, the miscible and immiscible blends are indicated by the open and closed symbols, respectively. The state of mixing of these blends was independent of composition and did not change with temperature, i.e. no *UCST* or *LCST*-type phase behaviour was observed. The symbol (+) refers to blends where refractive indices and T_g values for the two copolymers are too close to judge their state of mixing.

Blends of SMA48 with α-MSAN copolymers were also

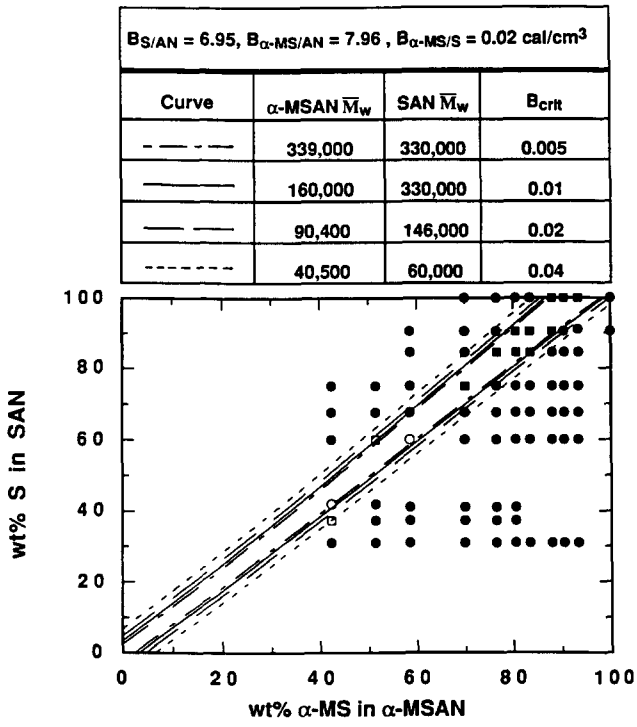

Figure 1 Miscibility map for 50/50 wt% blends of α-MSAN copolymers with SAN copolymers. Open and closed points refer to miscible and immiscible blends, respectively. The lines were calculated from equations (2) and (3) using the B_{ij} set and the constant values of B_{crit} tabulated. Point-by-point predictions of miscibility were made using this B_{ij} set and the actual molecular weights for each copolymer pair; circles denote pairs where this prediction matches the experimental observations while the squares denote pairs where the prediction does not match the experimental observations

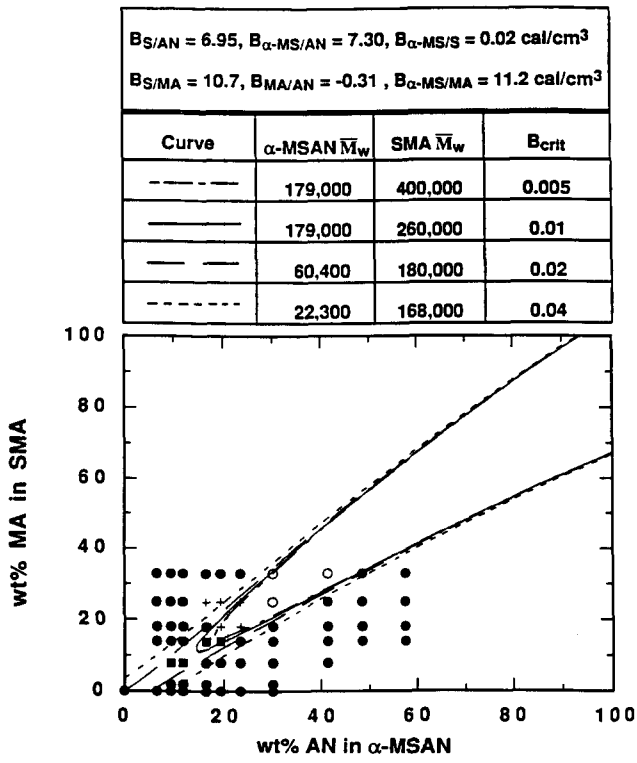

Figure 2 Miscibility map for 50/50 wt% blends of α-MSAN copolymers with SMA copolymers. The symbol (+) refers to blends where the T_g and refractive indices of the two copolymers are too close to judge whether these blends are miscible or immiscible. Lines and points have the same meaning as in *Figure 1*

examined; however, they were all found to be immiscible. Further analysis of these blends indicated that the SMA48, as prepared, had undergone hydrolysis as evidenced by an OH peak in the i.r. spectrum. Therefore, the results for blends containing SMA48 were not considered further. Since the tendency for MA to homopolymerize is very slight, copolymers containing higher MA levels are not formed[36–40]. Therefore, this map is restricted to the region of low MA content.

Theoretical interpretation and analysis

In principle, the composition map defining the boundaries between miscible and immiscible blends can be fitted to the Flory–Huggins theory combined with the binary interaction model to obtain information about the interaction energies that govern the phase behaviour. In terms of the Flory–Huggins theory, the free energy of mixing per unit volume is:

$$\Delta g_{mix} = RT\left[\frac{\phi_A \ln \phi_A}{\tilde{V}_A} + \frac{\phi_B \ln \phi_B}{\tilde{V}_B}\right] + B\phi_A\phi_B \qquad (1)$$

where R is the universal gas constant, T is the absolute temperature, and ϕ_i and $\tilde{V}_i$ are the volume fraction and molar volume of component i, respectively. For a binary blend of copolymer A composed of units 1 and 2 with another copolymer B composed of units 3 and 4, the net interaction energy density, B, according to the binary interaction model is given by:

$$B = B_{13}\phi'_1\phi''_3 + B_{14}\phi'_1\phi''_4 + B_{23}\phi'_2\phi''_3 + B_{24}\phi'_2\phi''_4 - B_{12}\phi'_1\phi''_2 - B_{34}\phi'_3\phi''_4$$

where the B_{ij} describe the interaction between the monomer unit pair i, j while ϕ'_i and ϕ''_i denote the volume fractions of i units in copolymers A and B. A stability analysis shows that the blend is miscible provided that B is less than a critical value, defined as:

$$B_{crit} = \frac{RT}{2}\left(\frac{1}{\sqrt{\tilde{V}_A}} + \frac{1}{\sqrt{\tilde{V}_B}}\right)^2 \qquad (3)$$

where $\tilde{V}_i$ is the molar volume of copolymers i.

The usual mapping procedure to obtain the set of B_{ij} values that best fits the above theory to the experimental miscibility region requires that the molecular weight of each copolymer is constant or that the molecular weights do not affect the miscibility behaviour significantly. The latter would be true if large negative B values exist within the miscibility zone. However, neither assumption is valid for the blend systems examined here. *Table 1* shows the B_{crit} for the various pairs of SAN and α-MSAN copolymers calculated from equation (3) using the measured weight-average molecular weights shown. There are relatively large variations in molecular weights within the SAN and α-MSAN copolymer series, and the B_{crit} for these copolymer pairs ranges from 0.008 to 0.056 cal cm^{-3}. Therefore, for this system, we cannot assume a constant B_{crit}, i.e. a constant molecular weight represents each component, to extract the binary interaction energies by the usual fitting of the theory to the copolymer–copolymer composition miscibility map.

All the B_{ij} values for this system have been estimated previously, and representative values are shown in *Figure 1*. The $B_{S/AN}$ and $B_{\alpha\text{-MS/AN}}$ values were obtained from analysis of phase diagrams of *LCST* types of blends of SAN copolymers or α-MSAN copolymers with

various homopolymers[18], while $B_{\alpha\text{-MS/S}}$ was deduced from critical molecular weight analysis of blends of PS with P(α-MS)[35]. All of these B_{ij} values were evaluated at 150°C. The interaction energy for the S/AN pair has been repeatedly confirmed in previous studies[18,19,34]. Cowie *et al.*[41] also reported an extensive study on blends of PS with P(α-MS) which led to the conclusion that $0.021 < B_{\alpha\text{-MS/S}} < 0.023$ cal cm^{-3}. *Figure 1* shows the miscibity region predicted using this set of interaction energies for four different sets of fixed molecular weights. The miscibility zone varies somewhat with the molecular weights chosen; however, none of the curves matches the experimentally observed miscibility region well. Blends of PS with α-MSAN copolymers are predicted to show a miscibility window at high α-MS content even in the limit of infinitely high molecular weights; however, this behaviour is not observed experimentally. The erroneously predicted miscibility window implies that the repulsive interaction energy, $B_{\alpha\text{-MS/AN}}$, used is too large. Since B_{crit} varies significantly from pair to pair for these copolymers, simple boundary curves are not adequate for comparing the observed state of miscibility with that predicted by this B_{ij} set. Instead, the prediction is made by comparing the B calculated from the B_{ij} set and equation (2) with B_{crit} computed from equation (3) (see *Table 1*) for each copolymer pair. In *Figure 1*, circles denote pairs where this prediction matches the experimental observations while squares indicate that the prediction does not match the experimental observations. On this basis, we conclude that this set of binary interaction energies does not adequately predict the state of miscibility for this blend system. Refinement of these parameters is examined next.

Considerable evidence supports the values of $B_{S/AN}$ and $B_{\alpha\text{-MS/S}}$ shown in *Figure 1*. Furthermore, reasonable variations of these parameters do not alter the predicted miscibility window significantly. The parameter that most influences the predicted miscibility region is $B_{\alpha\text{-MS/AN}}$. For example, lowering the value of $B_{\alpha\text{-MS/AN}}$ to 7.3 cal cm^{-3}, while retaining $B_{S/AN}$ and $B_{\alpha\text{-MS/S}}$ at the values previously used, gives a quite different prediction for the miscibility region for the four different sets of fixed molecular weights, as shown in *Figure 3*. This set of interaction energies predicts immiscibility for high contents of S and α-MS at high molecular weight limits, as observed experimentally. The size of the miscible zone varies considerably with B_{crit} or the choice of molecular weights within this range, and eventually vanishes in the infinitely high molecular weight limit. Again, none of these or other curves for B_{crit}=constant describes well the experimentally observed miscibility region, mainly because B_{crit} varies considerably from point to point in this diagram, as shown in *Table 1*. A point-by-point calculation using the actual molecular weights of the copolymers showed that this set of interaction energies correctly predicts the state of miscibility for most, but not all, pairs of copolymers. Of course, these predictions rely on the absolute accuracy of the molecular weight values used, most of which were determined by gel permeation chromatography calibrated by PS standards. In any case, this revised set of B_{ij} values better represents the miscibility behaviour for this blend system than the set previously used. These parameters are not yet known accurately enough for reliable prediction of complete phase diagrams for individual copolymer pairs.

The initial estimate of $B_{\alpha\text{-MS/AN}}$, 7.96 cal cm^{-3}, was

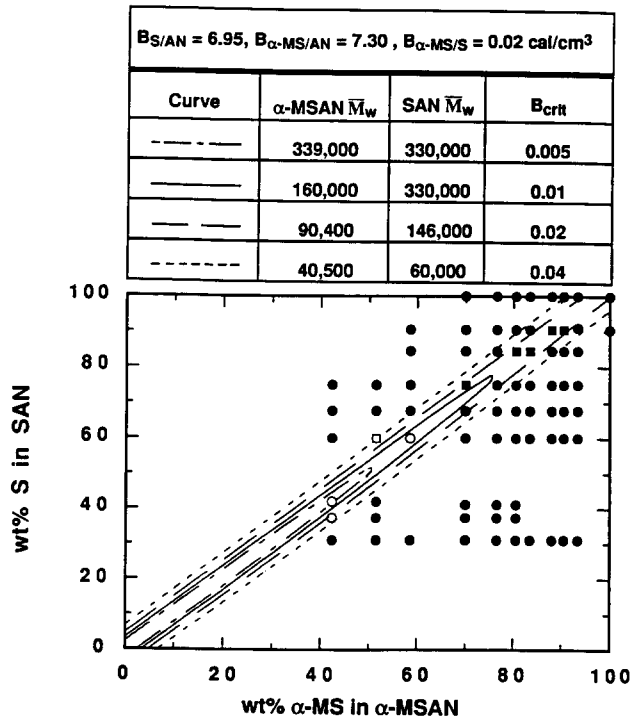

Figure 3 Miscibility map for 50/50 wt% blends of α-MSAN copolymers with SAN copolymers. Lines and points have the same meaning as in *Figure 1*

deduced from an analysis of the phase behaviour of blends of α-MSAN copolymers with various homopolymers[18]. A re-examination of these systems indicates that the revised value of 7.30 cal cm^{-3} for $B_{\alpha\text{-MS/AN}}$ is not inconsistent with these previous experimental results, particularly in view of possible error limits on other parameters used in these analyses.

A similar variation of molecular weight exists in *Figure 2* for the blends of α-MSAN copolymers with SMA copolymers. As seen in *Table 2*, the calculated B_{crit} ranges from 0.009 to 0.039 cal cm^{-3}. Most of the six binary interaction energies for the monomer unit pairs in this system have been estimated previously, e.g. the values of $B_{\alpha\text{-MS/S}}$, $B_{\alpha\text{-MS/AN}}$ and $B_{S/AN}$ were described above. The values for $B_{S/MA}$ and $B_{MA/AN}$ have been reported in a previous paper[30]. Our best estimates for these values are tabulated in *Figure 2*. The only interaction parameter about which there is no information is $B_{\alpha\text{-MS/MA}}$. The five B_{ij} for which values are available were inserted into equation (2), and the upper or lower limit on $B_{\alpha\text{-MS/MA}}$, needed to make the theoretical criteria for miscibility match the observed state of miscibility for every blend described in *Figure 2*, was calculated. From this analysis, the remaining parameter must lie in the following range: $11.1 < B_{\alpha\text{-MS/MA}} < 11.3$ cal cm^{-3}. *Figure 2* shows the theoretical miscibility regions calculated from the five known interaction energies and $B_{\alpha\text{-MS/MA}} = 11.2$ cal cm^{-3} for different fixed molecular weight combinations, i.e. constant B_{crit}. The predicted regions are quite sensitive to the molecular weights chosen, especially at low contents of AN and MA. Point-by-point comparisons of the experimental observations with the predictions using this B_{ij} set and the actual molecular weights are also shown in *Figure 2*. The agreement, while not perfect, is quite good.

Conclusions

Blends of α-MSAN with SAN copolymers are miscible so long as the AN content of each copolymer is about the same and is high enough. Blends of α-MSAN with SMA copolymers are miscible so long as the AN and MA contents are similar and high enough (of course, levels of MA higher than 50 mol% cannot be formed). The region of miscibility for the latter system seems to be broader than that of the former. The results indicate that the state of miscibility is rather sensitive to the molecular weight of these components for both systems. Because it is not practical to prepare such copolymers over a broad range of comonomer contents having very similar molecular weights, it is not possible to use the graphical maps of copolymer composition to display their miscibility/immiscibility behaviour or to extract interaction information in the typical ways that have emerged in recent years. In any case, the miscibility behaviour of blends of α-MSAN with both SAN and SMA copolymers can be reasonably described using the Flory–Huggins theory and the approximate set of B_{ij} values discussed here.

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