Miscibility in terpolymer–copolymer blends

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The phase behaviour of 50/50 blends of a series of terpolymers from styrene, maleic anhydride and acrylonitrile with styrene–acrylonitrile copolymers and styrene–maleic anhydride copolymers has been determined using the single glass transition temperature criterion. The appropriate expression for the overall blend interaction energy density according to the extended Flory–Huggins theory is examined and the general shapes of miscibility contours in composition space are deduced and presented in a novel manner. The experimental miscibility is dependent on both terpolymer and copolymer composition, and is well described by this expression using values of segmental interaction parameters available from the literature.

(Keywords: blends; terpolymer; copolymer)

INTRODUCTION

An effective first-order description of the free energy of mixing for two polymers is that given by the Flory–Huggins theory[1]:

$$\Delta G_m = RT(\phi_1 \ln \phi_1/V_1 + \phi_1 \ln \phi_2/V_2) + B\phi_1\phi_2 \quad (1)$$

where the ϕ_i are the polymer volume fractions and the V_i are the polymer molar volumes. The isothermal interaction energy density, B, is regarded as composition independent and effectively quantifies the enthalpic contribution to the free energy. Equation (1) is readily extended to cover cases where polymers 1 and 2 are both multicomponent copolymers by assigning individual segmental interaction energies B_{ij} which contribute to an overall energy density term, B_{blend} (a segment is normally defined to be a repeat unit)[2–4]. The contribution to B_{blend} from each i–j heterocontact is weighted by the volume fractions product of the contacting segments; this is positive for an *inter*copolymer contact and negative for an *intra*copolymer contact. So in general terms:

$$B_{blend} = \sum_{intra} \phi_i\phi_j B_{ij} - \sum_{intra} \phi_i\phi_j B_{ij} \quad (2)$$

Expression (2) has been used to good effect to describe the miscibility of many binary copolymer + copolymer and copolymer + homopolymer blends[5]. Not surprisingly terpolymer-based systems, in which there is a further element of composition variability, have received more limited attention, although the miscibility behaviour of methyl methacrylate–styrene–acrylonitrile terpolymers with several homopolymers and copolymers has been examined by two groups[6,7].

For blends involving terpolymers, the general equation (2) produces mathematically tractable forms only when the number of composition variables is restricted, such as cases where the blend components contain one or more comonomers in common. In this paper we report the miscibility of styrene–maleic anhydride–acrylonitrile (S-AN-MA) terpolymers with the styrenic copolymers, styrene–maleic anhydride (S-MA) and styrene–acrylonitrile (S-AN). If the terpolymer is indexed $A_xB_yC_{1-x-y}$ and the copolymer A_zC_{1-z}, then the particular form of equation (2) that follows is:

$$\begin{aligned} B_{blend} = {} & x(1-z)B_{AC} + yzB_{AB} + y(1-z)B_{BC} \\ & + z(1-x-y)B_{AC} - xyB_{AB} - x(1-x-y)B_{AC} \\ & - y(1-x-y)B_{BC} - z(1-z)B_{AC} \end{aligned} \quad (3)$$

Phase boundaries occur under critical conditions, i.e. when

$$f(x, y, z) = B_{blend} - B_{crit} = 0 \quad (4)$$

where the critical value of B is given by:

$$B_{crit} = (RT/2)(V_1^{-0.5} + V_2^{-0.5})^2 \quad (5)$$

Before examining the experimental data it is instructive to explore the possible phase behaviour, on the basis of equations (3) and (4), within x, y, z composition space. The most obvious presentation of the solutions to equation (4) is to indicate the phase boundaries on a triangular diagram, which describes the composition of the terpolymer $(x, y, 1-x-y)$, for constant values of the copolymer composition, z[6,7]. Such a diagram can be viewed generally as a section at z' on a triangular prism (see *Figure 1*), two of whose faces represent respectively the two binary copolymer mixtures which describe the limiting behaviour of the terpolymer–copolymer blends.

The right-hand face on *Figure 1* maps the miscibility of $A_xC_{1-x} + A_zC_{1-z}$, i.e. blends of different compositions of the same copolymer[8–10]. The one-phase area in such systems is symmetrical about the diagonal, and immiscibility occurs when the copolymers differ in composition by $\delta x = (B_{crit}/B_{AC})^{0.5}$. These blends display miscibility

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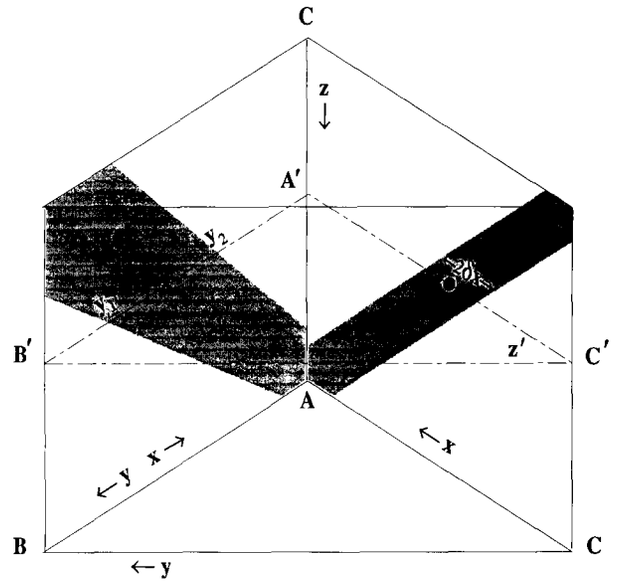

Figure 1 Schematic diagram of $A_xB_yC_{1-x-y}+A_zC_{1-z}$ terpolymer–copolymer composition space. Blends at $z=z'$ for all terpolymer compositions can be shown in the section A'B'C' of the prism outlined with the dashed line. The shaded areas are copolymer–copolymer miscibility regions as described in the text, y_1 and y_2 are the miscibility limits of A_xB_{1-x} with $A_{z'}C_{1-z'}$, and $2\delta x$ is the miscibility window for any $A_xC_{1-x}+A_zC_{1-z}$ blend. The solid circle on the diagonal of the right-hand face at $x=z'$ corresponds to the origin in *Figure 2*

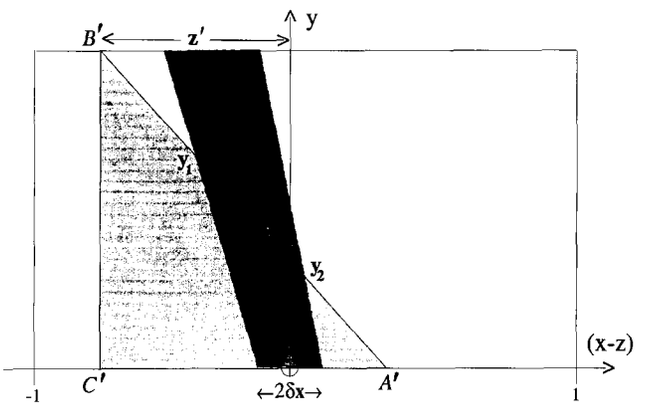

Figure 2 Schematic diagram of $A_xB_yC_{1-x-y}+A_zC_{1-z}$ terpolymer–copolymer composition space in the coordinate system $(z-x)$ *versus* y. The darker shaded area is the region where $B_{blend}<B_{crit}\sim 0.05\,J\,cm^{-3}$ for the representative values $a=40\,J\,cm^{-3}$, $b=1\,J\,cm^{-3}$ and $2h=20\,J\,cm^{-3}$ in equation (6). The lighter shaded triangle $A'B'C'$ is equivalent to the triangular section at A'B'C' in *Figure 1*

across the whole composition range for $B_{crit}>0$. In contrast, the behaviour of the common comonomer blend $A_xB_{1-x}+A_zC_{1-z}$ on the left-hand face may be less extensive. Although single-phase behaviour can occur across most of the composition space[11,12], generally forming a wedge-shaped area such as that shown in the figure extending from the origin to intersect with $y=1$, it may, for appropriate values of the B_{ij}, also fall within a closed semi-ellipse centred on the origin $(x,z)=(1,1)$. Phase boundaries of this latter type have been the subject of several previous publications[8,13–15]; in fact it may be shown generally that phase diagrams in x, y, z composition space which follow from equations (2) and (4) should also be bounded by some form of conic section. In the present case, a particularly useful expression results by restating B_{blend} in equation (3) alternatively as a function of only *two* composition variables $(x-z)$ and y. After some algebra, and setting $a=B_{AC}$, $b=B_{BC}$ and $h=(B_{AC}-B_{AB}+B_{BC})/2$, B_{blend} may be expressed as the general quadric surface:

$$B_{blend}=a(x-z)^2+2(x-z)yh+by^2 \qquad (6)$$

The condition $B_{blend}=B_{crit}$ describes the intersection of a horizontal plane with this surface to generate either an ellipse, a hyperbola or a pair of parallel/intersecting lines for, respectively, $(ab-h^2)<0$, $(ab-h^2)>0$ or $(ab-h^2)=0$. This is shown schematically for the second of these possibilities on the rectangular axes of *Figure 2*, where the B_{blend} axis is positive out of the plane of the paper. *Figure 2* is a phase diagram for all possible $A_xB_yC_{1-x-y}+A_zC_{1-z}$ blends in terms of y and the reduced composition variable $(x-z)$, and all miscible combinations are predicted to fall within the darker shaded area where $B_{blend}\leqslant B_{crit}$. The triangular composition section A'B'C' (at constant $z=z'$) shown in *Figure 1* is equivalent to the right-angled triangle $A'B'C'$ in *Figure 2* via the following transformation:

$$A'(x=1,\ y=0)\rightarrow A'[(x-z)=1-z',\ y=0]$$

$$B'(x=0,\ y=1)\rightarrow B'[(x-z)=-z',\ y=1]$$

$$C'(x=0,\ y=0)\rightarrow C'[(x-z)=-z',\ y=0]$$

Now all points on the diagonal of the right-hand face of *Figure 1* are at $(x=z,\ y=0)$ and so the solid circle shown in this figure forms the origin $((x-z),y)=(0,0)$ in *Figure 2*. Interestingly this also turns out to be the (only) stationary point on this quadric surface, obtained from the simultaneous conditions $\partial B_{blend}/\partial x=0$ and $\partial B_{blend}/\partial y=0$.

The intersection of the darker shaded area ($B_{blend}\leqslant B_{crit}$) of *Figure 2* with $A'B'C'$ is the predicted region of miscibility (for the representative values of B_{crit}, a, b and h given in the caption) for those terpolymer–copolymer blends where $z=z'$. Mapping this intersection back onto conventional triangular coordinates reveals the corresponding miscibility region in the terpolymer composition plane A'B'C' as a slightly distorted variant of that in the rectangular coordinate system of *Figure 2*. However, it is the latter (rectangular) form of presentation which we shall adopt here as it conveniently shows the miscibility of any $A_xB_yC_{1-x-y}+A_zC_{1-z}$ terpolymer–copolymer blend on a single diagram, rather than by a succession of triangular sections covering the composition range $0\leqslant z\leqslant 1$. Triangular sections A'B'C' for any value of $z=z'$ may be obtained by displacing $A'B'C'$ by a distance z' along the $(x-z)$ axis of *Figure 2*.

EXPERIMENTAL

S-AN-MA terpolymers were prepared by solution polymerization using methyl ethyl ketone in an all-glass reactor using bis-(2-ethylhexyl)peroxydicarbonate as free-radical initiator. Polymerization temperature was 63°C except for samples SM 3 and SM 49-1 where 70°C and 55°C were used, respectively. Conversions were kept low to limit composition drift. The S-AN samples of known composition were obtained from commercial suppliers and the S-MA copolymers were provided by DSM. Terpolymer and copolymer details are summarized in *Tables 1* and *2*.

Molar masses were established by gel permeation chromatography (using tetrahydrofuran solutions) in terms of standard polystyrene equivalents. B_{crit} values

Table 1 Characteristics of S-AN and S-MA copolymers

Supplier (code)	Copolymer (wt% AN and MA)	Styrene (volume fraction)	T_g (°C)	$10^4 M_w$ (g mol^{-1})	M_w/M_n
JSR(AS230)	S-AN(26)	0.75	104	13.5	1.8
JSR(AS240)	S-AN(29)	0.72	104	15.2	1.8
BASF(RZ035)	S-AN(33)	0.68	104	10.2	2.1
–[a]	S-MA(28)	0.80	161	11.0	~2
–[a]	S-MA(32)	0.77	170	11.0	~2
–[a]	S-MA(36)	0.74	174	6.5	2.6

[a] Prepared by Dr Klumperman

Table 2 Characteristics of S-AN-MA terpolymers

Terpolymer code	Styrene (volume fraction)	Acrylonitrile (volume fraction)	T_g (°C)	$10^4 M_w$ (g mol^{-1})	M_w/M_n
SM 41-8	0.72	0.21	135	8.9	2.1
SM 43	0.63	0.20	154	14.0	1.7
SM 41-2	0.67	0.16	157	13.0	1.8
SM 4	0.77	0.05	159	9.2	1.7
SM 3	0.78	0.02	158	7.3	1.8
SM 39	0.71	0.09	163	12.0	1.8
SM 23	0.68	0.10	171	9.0	1.9
SM 49.1	0.66	0.12	174	5.2	3.5[a]

[a] This sample contained a low molar mass fraction

Table 3 Values of the interaction energy densities used

i–j	B_{ij} (J cm^{-3})
S-AN	22.8
S-MA	40.0
MA-AN	1.0

were calculated from molar masses using a group additivity scheme to estimate copolymer and terpolymer molar volumes[16]. Although these varied from blend to blend, the sizes of the calculated areas of miscibility described below were not especially sensitive to this parameter and an average value of $B_{crit} = 0.045$ J cm^{-3} was deemed perfectly adequate to describe all blends.

Blends were prepared by codissolving 50/50 wt% samples in methyl ethyl ketone followed by precipitation into isopropanol or hexane. Blend glass transition (T_g) values were obtained using a Perkin–Elmer DSC 7 calorimeter, at a scanning rate of 10°C min^{-1} between 40 and 250°C. The T_g values were taken as those displayed on the second run and the criterion for a one-phase blend was the occurrence of a single T_g.

RESULTS AND DISCUSSION

The experimental data for the terpolymer–copolymer blend system $S_xAN_yMA_{1-x-y}+S_zMA_{1-z}$ are shown in *Figure 3* using the coordinate system described above. The position of a blend is determined by the terpolymer AN volume fraction (y) and the difference between the styrene volume fraction of the terpolymer and the styrene volume fraction in the copolymer. Thus each horizontal band of data points with constant y value arises from blends of copolymers of different compositions with an individual terpolymer; for example the miscible combination SM 4 + S-MA(28) is plotted at $(x-z) = (0.77-0.80) = -0.03$ and $y = 0.05$. *Figure 4* gives the corresponding data for $S_xMA_yAN_{1-x-y}+S_zAN_{1-z}$ where in this case the y is the MA volume fraction in the terpolymer.

To predict phase boundaries from equation (6), the same three B_{ij} interaction values are required for each system, namely $B_{S\text{-}AN}$, $B_{S\text{-}MA}$ and $B_{MA\text{-}AN}$. The first of these, $B_{S\text{-}AN} = 22.8$ J cm^{-3}, has been established previously[8,12,14]. The S-MA and MA-AN interactions have also been determined, but in terms of the Flory χ-parameter, by Aoki[17] from an examination of the phase diagram of the binary copolymer blend S-AN + S-MA. The formal transformation between χ and B requires the value of the lattice reference volume V_{ref}[1,6,14]. Here we chose to circumvent the problems associated with the choice of an appropriate V_{ref} in systems made up from monomer repeat units of disparate sizes by reassessing

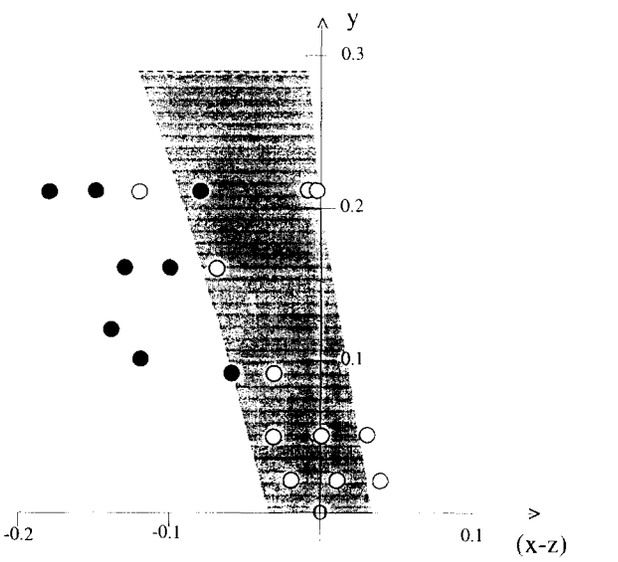

Figure 3 Shaded area is the predicted region for miscible $S_xAN_yMA_{1-x-y}+S_zMA_{1-z}$ blends calculated from equations (4) and (6) with $B_{crit} = 0.045$ J cm^{-3} and the interaction parameter values in *Table 3*. Solid circles are two-phase blends, open circles are single-phase blends

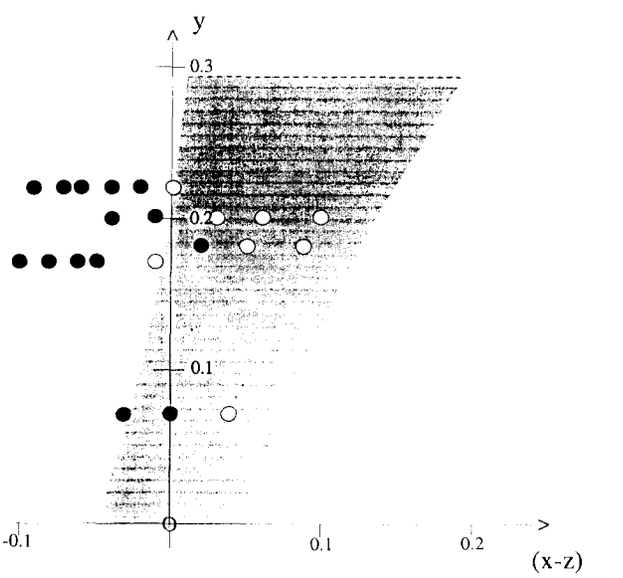

Figure 4 Shaded area is the predicted region for miscible $S_xMA_yAN_{1-x-y}+S_zAN_{1-z}$ blends calculated from equations (4) and (6) with $B_{crit} = 0.045$ J cm^{-3} and the interaction parameter values in *Table 3*. Solid circles are two-phase blends, open circles are single-phase blends

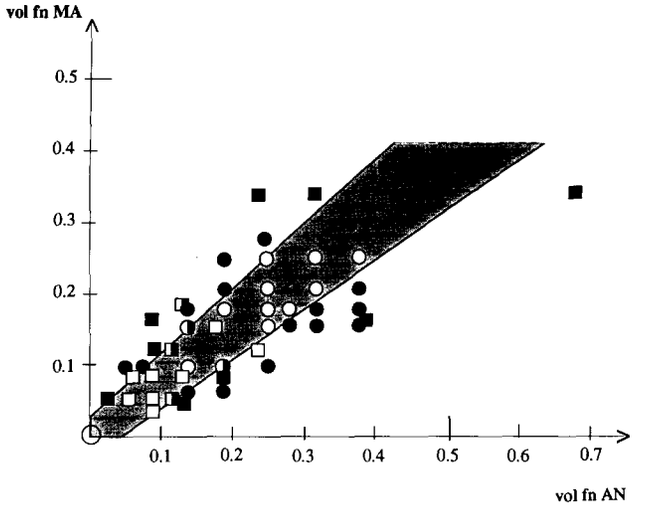

Figure 5 Miscible (open symbols), immiscible (solid symbols) and part-miscible (half-solid symbols) blends of S-AN and S-MA copolymers according to reference 17 (circles) and reference 18 (squares). The shaded wedge-shaped area represents the chosen best fit to the data and generates the interaction parameter values listed in *Table 3*

the phase data of Aoki, which we have combined with data collected by Kim *et al.*[18] for the same system, as shown in *Figure 5*. This yields the B_{ij} data summarized in *Table 3* using the procedures for fitting such binary copolymer phase diagrams which have been fully described elsewhere[11,12]. (*Figure 5* is of course an experimental realization of the left-hand face of the general description given in *Figure 1*.)

Using the B_{ij} values in *Table 3* and $B_{crit}=0.045\ J\ cm^{-3}$, equation (6) then predicts miscibility to occur within the shaded truncated wedge-shaped areas shown in *Figures 3* and *4* respectively. (This prediction is easily made by solving the quadratic resulting from equation (6) under the conditions of constant y and $B_{blend}=B_{crit}$, for $-1\leqslant z\leqslant 1$.) Experimentally, most of the miscible blends do indeed fall within these predicted miscibility areas, thus it appears that the simple extended Flory–Huggins theory does provide a useful representation of the mixing thermodynamics in terpolymer–copolymer systems.

As elaborated above, the edges of a conventional triangular diagram show the miscibility limits of the related copolymer–copolymer blends for a given value of the composition variable z. These same limits ($2\delta z$ and (y_1-y_2)) are correspondingly located on the sides ($A'C'$ and $A'B'$) of triangle $A'B'C'$ of *Figure 2*, where they intersect the shaded region $B_{blend}<B_{crit}$. It was noted above that there is only one stationary point on the quadric B_{blend} surface (in the triangular representation at the solid circle in *Figure 1*, or alternatively at the origin of the rectangular axes in *Figure 2*). This, taken with an evaluation of the curvature over the entire quadric surface, reveals that single-phase terpolymer–copolymer blends will always occur if the constituent copolymer–copolymer blends are miscible, and moreover the miscible terpolymer blends will be located about a composition axis linking the single-phase regions of the constituent copolymer–copolymer systems. (If the copolymer–copolymer miscibility regions become very small as $B_{crit}\rightarrow 0$ then terpolymer–copolymer miscibility may be molecular-weight limited.) It should be noted, however, that this condition holds generally *only* where the blend components have two comonomers in common, and so limits the usefulness of observations on copolymer–copolymer systems as a guide to potentially miscible terpolymer–copolymer blends.

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