Phase behaviour of blends of poly(methyl methacrylate) with poly(styrene-*co*-methacrylonitrile)

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The phase behaviour of blends of poly(methyl methacrylate) (PMMA) with poly(styrene-*co*-methacrylonitrile) (SMAN) was investigated using differential scanning calorimetry. PMMA is miscible with SMAN having methacrylonitrile (MAN) contents between 8 and 63 wt%. The miscibility range is wider than that of PMMA/poly(styrene-*co*-acrylonitrile) blend system, and is in good agreement with that predicted using a non-hydrogen-bonded solubility parameter approach. Segmental interaction parameters involving MAN are smaller than corresponding parameters involving acrylonitrile.

(Keywords: miscibility; poly(methyl methacrylate); poly(styrene-*co*-methacrylonitrile); phase behaviour; blends)

Introduction

Poly(*n*-alkyl methacrylate)s such as poly(methyl methacrylate) (PMMA), poly(ethyl methacrylate) (PEMA) and poly(*n*-propyl methacrylate) (P*n*PMA) are miscible with poly(styrene-*co*-acrylonitrile) (SAN) over certain copolymer composition ranges, showing 'miscibility windows'[1–4]. The width of the miscibility window decreases in the order PMMA > PEMA > P*n*PMA. However, poly(*n*-butyl methacrylate) (P*n*BMA) is immiscible with SAN[2]. Our recent study has shown that binary blends of poly(*p*-methylstyrene-*co*-acrylonitrile) (*p*MSAN) with PMMA, PEMA, P*n*PMA and P*n*BMA also show miscibility windows[5]. For P*n*BMA/*p*MSAN blends, the window is very narrow. Cowie and Elexpuru[6] have recently reported that miscibility windows also exist for binary blends of poly(α-methylstyrene-*co*-acrylonitrile) (αMSAN) with PMMA, PEMA, P*n*PMA and P*n*BMA, and the miscibility window for P*n*BMA/αMSAN blends is also very narrow. We are now studying the miscibility behaviour of methacrylonitrile (MAN)-containing polymers. In this communication, we report the miscibility of PMMA with poly(styrene-*co*-methacrylonitrile) (SMAN).

Experimental

Materials. SMAN samples of varying compositions were prepared by free radical polymerization in 2-butanone at 80°C initiated by azobisisobutyronitrile (AIBN). The monomer:solvent volume ratio was 1:2.5; the AIBN concentration was 3.5 $\text{mmol}\,\text{l}^{-1}$. The copolymers were recovered by precipitation from solutions into excess methanol. Conversions were about 20–30%. The MAN contents of copolymers were determined by elemental analysis of nitrogen. In the following discussion, the number after SMAN denotes the weight percentage of MAN in the copolymer. *Table 1* shows the characteristics of the copolymers. The glass transition temperatures (T_gs) of various copolymers are in the range 96–108°C, which are close to those of polystyrene (100°C) and poly(methacrylonitrile) (PMAN) (108°C). PMMA was similarly prepared by free radical polymerization.

Preparation of blends. Various PMMA/SMAN blends in weight ratios of 1:3, 1:1 and 3:1 were prepared by solution casting from tetrahydrofuran at room temperature. The cast films were then dried *in vacuo* at 90°C for at least 1 week.

Blend miscibility. The miscibility of various blends was ascertained using the single T_g criterion. T_g measurements were made with a Perkin–Elmer DSC-4 differential scanning calorimeter using a heating rate of 20°C min^{-1}. Since the T_g of PMMA is only 10–20°C higher than those of SMAN samples, the blends were subjected to an annealing process. The value of annealing in ascertaining the miscibility of blends containing two polymers with similar T_g values has been well documented[5–11]. Each of the blends was first kept in the instrument at 135°C for 5 min and then annealed at 65°C for 10 days. The annealed sample was then scanned through the glass transition region. The appearance of a single enthalpy recovery peak is indicative of miscibility.

Cloud point measurements. All the miscible blends were examined for the existence of lower critical solution

Table 1 Characteristics of polymers

Polymer	T_g (°C)	M_n (kg mol^{-1})	M_w/M_n
SMAN3.9	97	24.3	1.78
SMAN5.6	96	22.0	1.68
SMAN10.2	96	14.7	1.70
SMAN17.1	96	21.9	1.78
SMAN27.3	97	18.0	2.33
SMAN35.4	103	21.3	2.22
SMAN40.1	105	17.9	2.33
SMAN46.6	106	18.7	2.15
SMAN53.0	107	15.7	2.03
SMAN57.8	108	15.4	1.80
SMAN62.8	106	18.8	1.42
SMAN68.7	108	13.8	1.56
PMMA	119	63.6	1.70

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Table 2 Characteristics of PMMA/SMAN blends (applicable to all three blend compositions)

Copolymer	Clarity	No. of T_gs	*LCST* behaviour
SMAN3.9	Hazy	2	–
SMAN5.6	Hazy	2	–
SMAN10.2	Clear	1	No
SMAN17.1	Clear	1	No
SMAN27.3	Clear	1	No
SMAN35.4	Clear	1	No
SMAN40.1	Clear	1	No
SMAN46.6	Clear	1	Yes
SMAN53.0	Clear	1	Yes
SMAN57.8	Clear	1	Yes
SMAN62.8	Clear	2	Yes
SMAN68.7	Hazy	2	–

temperature (*LCST*) behaviour using the method described previously[11]. The temperature at which the transparent film first developed cloudiness upon heating was taken as the cloud point.

Results and discussion

Table 2 summarizes the optical appearance, the number of glass transitions and the existence of *LCST* behaviour of the blends.

Blends of PMMA with SMAN3.9 and SMAN5.6 were hazy. Each of the annealed blends showed two enthalpy recovery peaks, indicating that PMMA is immiscible with these SMAN samples. Blends of PMMA with SMAN having MAN contents between 10.2 and 57.8 wt% were clear. Each of the annealed blends showed only one enthalpy recovery peak, confirming that PMMA is miscible with these SMAN samples. Blends of PMMA with SMAN46.6, SMAN53.0 and SMAN57.8 showed *LCST* behaviour but the other miscible blends remained clear up to 300°C, the highest temperature attained by the apparatus. Blends of PMMA with SMAN62.8 were clear, but each of the annealed blends showed two enthalpy recovery peaks. It was believed that these blends might have low *LCST*s such that the initial treatment at 135°C had induced phase separation. Indeed, when the clear blends were examined for *LCST* behaviour, they turned cloudy at 115–120°C. Nonetheless, the low *LCST* values indicate that the blends are near the miscibility boundary. Blends of PMMA with SMAN68.7 were hazy and each blend showed two T_gs, indicating the immiscibility of these blends.

The present results show that PMMA is miscible with SMAN over a copolymer composition range of 8–63 wt% MAN. The phase diagram is shown in *Figure 1*. In comparison, the lower end of the miscibility limit for PMMA/SAN blends is at about 9 wt% acrylonitrile (AN) and the higher end is in the range 30–39 wt% AN[1–3]. Thus the miscibility range of PMMA/SMAN blends is much wider than that of PMMA/SAN blends.

The miscibility of homopolymer A/copolymer BC blends is commonly explained by a binary interaction model[12–14]. Although homopolymer A is immiscible with either homopolymer B or homopolymer C, it can be miscible with copolymer BC if the intramolecular 'repulsive' interaction between the two types of segments in the copolymer is sufficiently strong. Based on the binary interaction model, the interaction parameter χ_{blend} for the present blend system is related to three segmental interaction parameters by:

$$\chi_{\text{blend}} = y\chi_{\text{MMA/MAN}} + (1-y)\chi_{\text{S/MMA}} - y(1-y)\chi_{\text{S/MAN}}$$

where y is the volume fraction of MAN in the copolymer. At the miscibility–immiscibility boundary, χ_{blend} equals χ_{crit} which is related to the degrees of polymerization N_i of the two component polymers by:

$$\chi_{\text{crit}} = 1/2(N_1^{-1/2} + N_2^{-1/2})^2$$

The N values for PMMA and SMAN are taken to be 640 and 250, leading to a value of 0.0053 for χ_{crit}. The miscibility limits are considered at 8 and 63 wt% MAN, corresponding to y values of 0.077 and 0.62, respectively. Since $\chi_{\text{S/MMA}}$ is 0.030, $\chi_{\text{MMA/MAN}}$ and $\chi_{\text{S/MAN}}$ are then 0.19 and 0.52, respectively, which are smaller than the values of 0.46 and 0.829 for $\chi_{\text{MMA/AN}}$ and $\chi_{\text{S/AN}}$, respectively[3]. The smaller values of $\chi_{\text{MMA/MAN}}$ and $\chi_{\text{S/MAN}}$ are expected in view of the relation between χ and the solubility parameters (δ) of the polymers, namely:

$$\chi = V(\delta_1 - \delta_2)^2/RT$$

where V is a reference volume, commonly taken as the molar volume of the smallest polymer repeat unit. The δ value of poly(methacrylonitrile) [24.3 $(\text{J cm}^{-3})^{1/2}$] is smaller than that of poly(acrylonitrile) [27.4 $(\text{J cm}^{-3})^{1/2}$][15,16]. Thus the segmental interaction parameters involving MAN are expected to be smaller than those parameters involving AN.

Coleman *et al.*[15,16] have recently suggested that the miscibility window phenomenon in homopolymer/copolymer blends can be explained by a non-hydrogen-bonded solubility parameter (δ) approach. Since the δ value of a copolymer varies with its composition, there will be a range of compositions over which the δ values of copolymers are closely matched to that of the

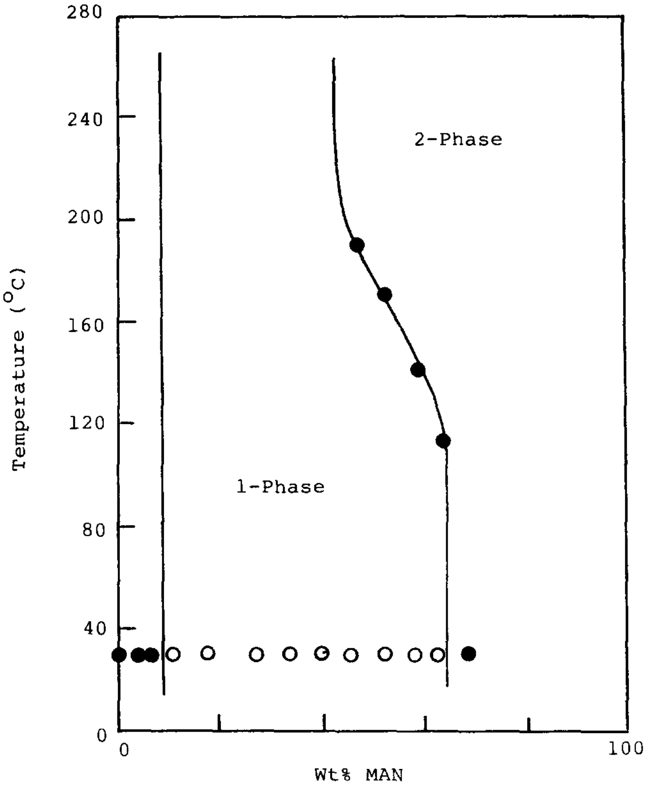

Figure 1 Phase diagram of PMMA/SMAN (1:1) blends. (○) miscible blends; (●) immiscible blends

homopolymer, giving rise to miscibility. Coleman *et al.*[16] used this approach to predict the miscibility ranges of some poly(methacrylate)/SAN blends and the results were in reasonably good agreement with the experimental values. The δ value of PMMA is 18.4 $(\mathrm{J\,cm^{-3}})^{1/2}$ and those of SMAN and SAN are in the range 19.4–24.3 and 19.4–27.4 $(\mathrm{J\,cm^{-3}})^{1/2}$, respectively[16]. From these δ values alone, PMMA/SMAN blends are expected to show a wider miscibility window than PMMA/SAN blends. The miscibility range for PMMA/SMAN blends is predicted to be 2–60 wt% MAN, using computer software developed by Coleman *et al.*[16] and assuming a moderate hydrogen-bonding interaction. The predicted range is in good agreement with our observed range. However, it should be noted that the predicted miscibility range using the δ approach depends on the choice of the type of intermolecular interaction. In this case, the choice of a moderate hydrogen-bonding interaction gives the best result.

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