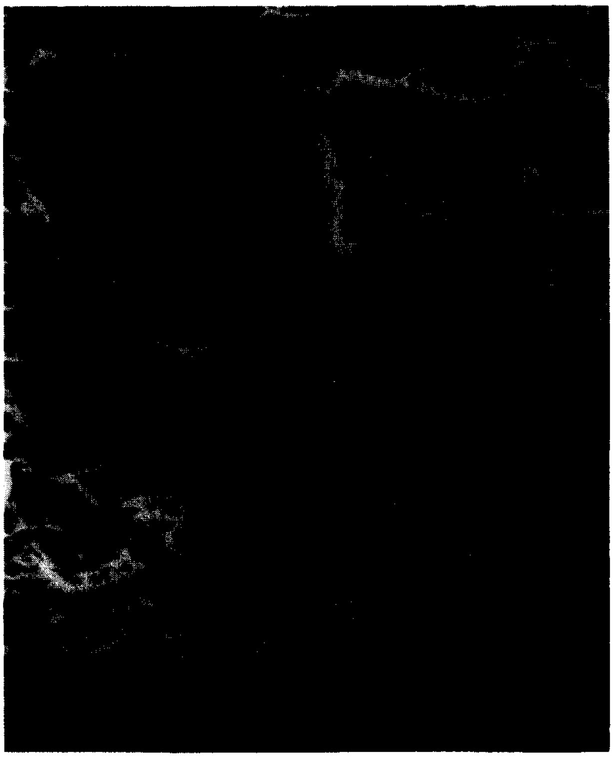

Figure 5 High magnification SEM micrograph of portion of fracture surface near edge of water-soaked sample

CONCLUSION

Small quantities of water enter the structure of extruded PS at temperatures well below T_g. The response to tension is consistent with a mild plasticizing action by the absorbed water. Microcrazes result in a crazing yield somewhat similar to the stress whitening of HIPS.

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Miscibility of SAN with polyacrylates and polymethacrylates

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Styrene–acrylonitrile copolymers, SAN, are known to be miscible with poly(methyl methacrylate). Based on the presence of a single composition dependent glass transition and lower critical solution temperature behaviour, it is shown that SAN is also miscible with poly(ethyl methacrylate). However, the SAN does not appear to be miscible with other polymethacrylates or polyacrylates.

Keywords Blends; miscibility; glass transition; lower critical solution temperature; poly(ethyl methacrylate); styrene–acrylonitrile copolymer

INTRODUCTION

It has been known for some time that styrene–acrylonitrile copolymers, SAN, and poly(methyl methacrylate), PMMA, are miscible$^{1-4}$. Recently, it was observed in this laboratory that poly(α-methyl styrene-co-acrylonitrile), αMSAN, is miscible with PMMA and PEMA, poly(ethyl methacrylate), but not with higher homologues^5. This raises the question of whether SAN might be miscible with PEMA or other related polymers. To answer this, two polyacrylates, PMA and PEA, four polymethacrylates, PEMA, PnPMA, PiPMA and PCHMA, as well as PVAc, which has reversed carbonyl group position to PMA, were blended with SAN. The appearance of the cast films and glass transition temperature behaviour were used to judge miscibility. Further measurements of density, the change in heat capacity at the glass transition, and lower critical solution temperature, *LCST*, behaviour were made for miscible blends.

EXPERIMENTAL

The source of the polymers used in this work are listed in *Table 1*. Blends containing different weight percentages of SAN were prepared by solution casting from tetrahydrofuran, THF. Each polymer was first dissolved in THF at the 5 to 10% level and then mixed in proper proportions. After vigorous stirring for a few hours, the mixture was poured into aluminium pans wrapped by aluminium foil punched with pin-holes to evaporate the solvent slowly. The resulting films were dried in vacuum at room temperature for one day and then at 60°C and 110°C for 3 days at each temperature.

The glass transition temperature of the polymers and

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Table 1 Polymers used in experimental study

Polymer	Abbreviation	Source	Molecular weight	Ref.
Poly(styrene–co-acrylonitrile) 28% AN by wt.	SAN	RMD-4511 (Union Carbide)	$\bar{M}_n$ = 88600 $\bar{M}_w$ = 223000 $\bar{M}_z$ = 679600	3
Poly(methyl acrylate)	PMA	Celanese Chemical Co.	$\bar{M}_w$ = 576000	5
Poly(ethyl acrylate)	PEA	Celanese Chemical Co.	$\bar{M}_w$ = 137000	5
Poly(ethyl methacrylated)	PEMA	Elvacite 2042 (DuPont)	$\bar{M}_w$ = 438000	5
Poly(n-propyl methacrylate)	PnPMA	Polysciences Inc.	$[\eta]$ = 2.00 dl/g (in 2-butanone, 25°C)	5
Poly(isopropyl methacrylate)	PiPMA	Polysciences Inc.	$[\eta]$ = 2.30 dl/g (in 2-butanone, 25°C)	5
Poly(cyclohexyl methacrylate)	PCHMA	PRD-6 (Rohm & Haas)	$\bar{M}_w$ = 492000	5
Poly(vinyl acetate)	PVAc	AYAF (Union Carbide)	$\bar{M}_w$ = 124000	5

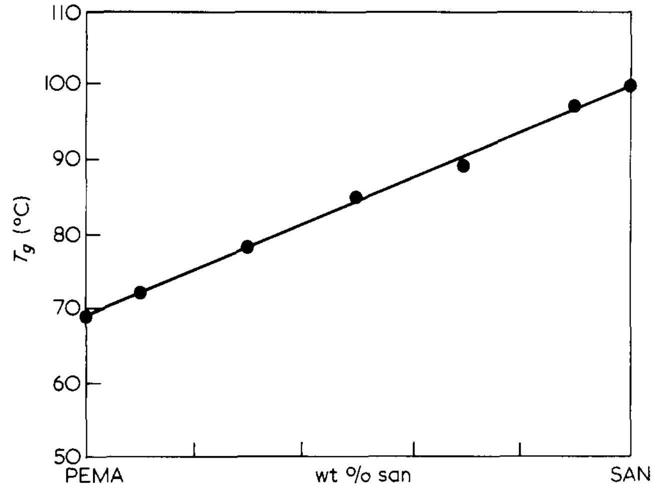

Figure 1 Glass transition behaviour of SAN–PEMA mixtures

blends were measured using a Perkin-Elmer DSC-2 differential scanning calorimeter equipped with a Thermal Analysis Data Station (TADS). The heating rate was 10°C/min for all samples. The T_g was taken as the onset of the change of slope in the heat capacity plot determined by extrapolating both slopes to the point of intersection. The change in specific heat was taken as the shift in baseline during the transition.

The densities of cast films were measured with an analytical balance using n-heptane as the buoyant fluid. The cast films were weighed in air and then in n-heptane. The buoyance force differences were used to calculate the specific volumes and densities.

The apparatus and experimental conditions used in the cloud point observations to establish *LCST* behaviour were described in detail elsewhere[3]. The temperature at which the transparent film first became opalescent on heating was taken as the cloud point.

RESULTS AND DISCUSSION

PEMA/SAN blends

The cast PEMA–SAN films were transparent, and with d.s.c. showed a single glass transition temperature for each composition. Both facts provide evidence that mixtures of PEMA and SAN are completely miscible. *Figure 1* shows that T_g is essentially linear in blend composition when expressed on a weight basis. Owing to the similar densities of these two polymers, an analogous plot based on volume fraction would also be linear. The values of the observed glass transitions were strongly dependent on the history of the sample prior to thermal analysis measurement especially for those with high PEMA content. For example, a PEMA sample cast from solution and dried for only one day at 110°C exhibited a T_g of 60°C as compared to 69°C for similar samples dried at this temperature for three days. This is the result of slow removal of residual solvent. Higher temperatures for drying can result in monomer generation by depolymerization which also decreases T_g by plasticization. Thus, considerable care must be exercised for this system to obtain a T_g not affected by residual volatiles. We believe that the results shown in *Figure 1* are relatively free of this effect.

Each of the PEMA–SAN blends exhibited phase separation on heating indicating *LCST* behaviour (see *Figure 4*). The cloudiness which developed on heating was not reversed on cooling owing to the low segmental mobility inherent to the close proximity of the cloud point curve to the glass transition of these blends. For purposes of comparison, cloud points for related systems reported in the literature are also shown in *Figure 4*. Identification of the polymers involved in this comparison is given in *Table 2*. Owing to the complexity of these curves and differences in molecular weight of the various polymers involved in this comparison, it is not possible to make definitive conclusions concerning the role of molecular structure on the temperature levels at which phase separation occurs. Other studies are needed to isolate the effects attributable to molecular structure alone.

The densities of PEMA–SAN blends were measured as described above and are shown in *Figure 2*. The linear relationship of density indicates that the excess volume of mixing for this system is essentially zero within the limits of experimental error. The change in heat capacity, ΔC_p, at the glass transition, as shown in *Figure 3*, is a linear function of blend composition, within experimental error, connecting values for pure SAN of 0.10 cal/g°C and pure PEMA of 0.056 cal/g°C.

Blends of SAN with other polymers

Blends of SAN with PMA, PEA, PVAc, PiPMA, PnPMA and PCHMA respectively from 10 to 90 wt%

Table 2 Information on polymers used in comparisons made in *Figure 4*

Polymer	Abbreviation	Source	Molecular weight	Ref.
Poly(α-methyl styrene–co-acrylonitrile)	αMSAN	Luran KR 2566U (BASF)	$\bar{M}_n$ = 57 000 $\bar{M}_w$ = 160 000	5
Poly(methyl methacrylate)	PMMA	V-415 (Rohm & Haas)	$\bar{M}_w$ = 191 000	5

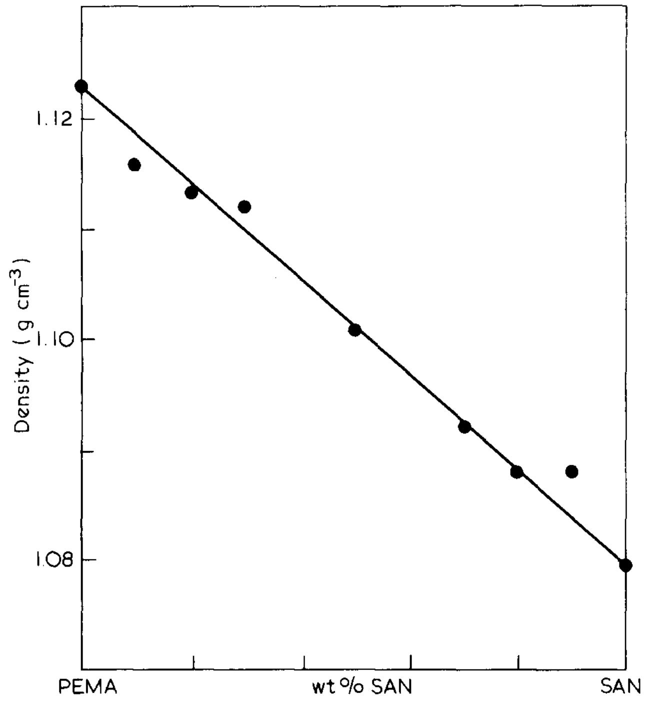

Figure 2 Density of SAN–PEMA blends

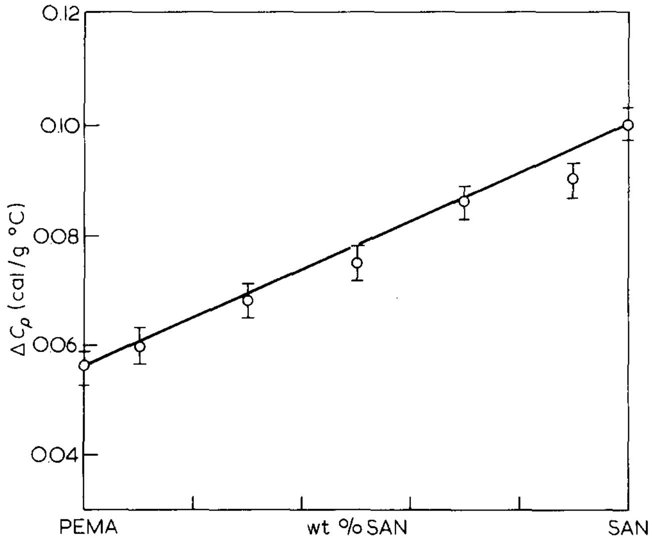

Figure 3 Change in heat capacity at the glass transition for SAN–PEMA blends

compositions were found to be cloudy or heterogeneous. D.s.c. showed two glass transition temperatures for each blend except for mixtures of SAN and PCHMA which have nearly the same T_g which cannot be distinguished by d.s.c. The cloudy appearance of these blends indicates immiscibility.

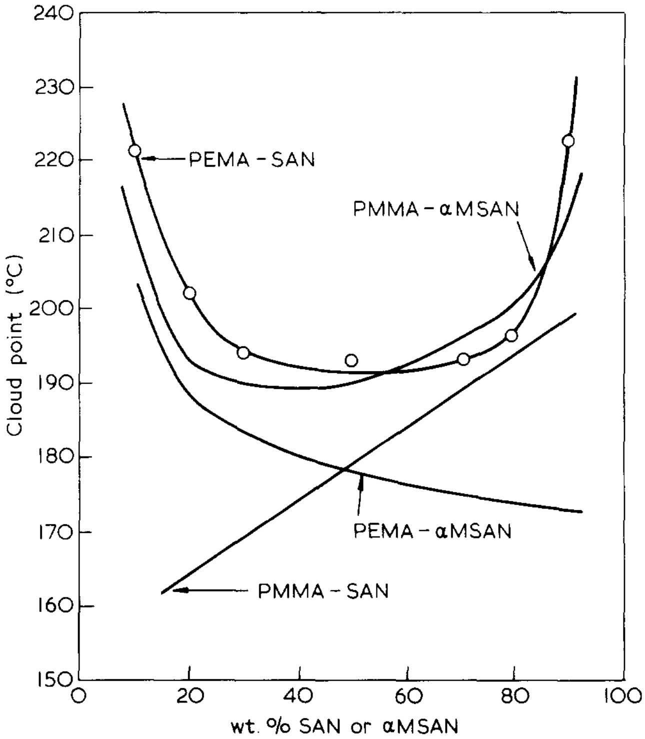

Figure 4 Cloud points for SAN–PEMA blends and comparisons with related systems[3,5]

CONCLUSION

This work has shown that SAN is miscible with PEMA but not with its higher alkyl homologues. The polyacrylates, PMA and PEA, were found to be immiscible with SAN. Changing the carbonyl group position from that in PMA to that in PVAc does not result in miscibility with SAN.

The linear additivity of T_g, ΔC_p and ρ in PEMA–SAN blends is similar to that observed for the PMMA–SAN system[4]. *LCST* behaviour is seen for all four of these related systems, PMMA with SAN and αMSAN and PEMA with SAN and αMSAN[5].

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