The miscibility window of poly(methylmethacrylate)/poly(styrene-*co*-acrylonitrile) blends

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The miscibility behaviour of poly(methylmethacrylate)/poly(styrene-*co*-acrylonitrile) (PMMA/SAN) blends with changes in blend ratio and acrylonitrile content of SAN was investigated by laser light scattering. The results show a miscibility window in the temperature *versus* copolymer composition plane. The phase morphology was observed over the whole copolymer composition and temperature area by light microscopy. A highly interconnected two-phase structure which occurs just above the lower critical solution temperature can also be found at room temperature in a certain region just outside the composition of the miscibility window. The differential scanning calorimetry trace of miscible systems displays a broadening at high PMMA contents in the blend.

(Keywords: blends; poly(methylmethacrylate); poly(styrene-*co*-acrylonitrile); light scattering; glass transition temperature)

INTRODUCTION

In recent years, there has been a great deal of interest in studies of the phase behaviour of polymer blends[1-5]. Especially, blends consisting of a homopolymer and a random copolymer or two copolymers represent an interesting class of systems due to the so-called 'repulsion effect'[3]. According to this effect, miscibility can occur in the absence of specific intermolecular interactions. For a blend of a homopolymer (A) and a random copolymer (B), where A consists of segments of type 1 and B of segments of types 2 and 3, the interaction parameter X_{AB} can be expressed in terms of the respective segmental interaction parameters[1,2,4]:

$$X_{AB}=\beta\chi_{12}+(1-\beta)\chi_{13}-\beta(1-\beta)\chi_{23} \qquad (1)$$

where β represents the mole fraction of component 2 in the random copolymer, Miscibility is only to be expected if $X_{AB}<0$. In the case $0<\chi_{12}\lesssim\chi_{13}<\chi_{23}$ the repulsion between the different segments comprising the copolymer is stronger than the repulsions between the homopolymer and copolymer segments. Therefore, the miscibility in a certain range of copolymer composition does not originate from any specific interactions but arises from the special structure of X_{AB} given by equation (1).

Generally, these systems display lower critical solution temperature (*LCST*) behaviour. Representing the phase behaviour of homopolymer/copolymer blends in the temperature–copolymer composition plane, one gets a so-called 'miscibility window'. The window of miscibility in a homopolymer/copolymer blend was first observed for the system poly(2,6-dimethyl-1,4-phenylene oxide)/poly(*para*-chlorostyrene-*co*-*ortho*-chlorostyrene) (PPO/P(*p*CS-*co*-*o*CS))[5]. A similar behaviour is known for the system poly(methylmethacrylate)/poly(styrene-*co*-acrylonitrile) (PMMA/SAN), which should be miscible in the range from 9 up to 26.5 wt% of AN in SAN[6].

Owing to the small difference in the glass transition temperatures (T_g) of PMMA and SAN, it is impossible to extract the window of miscibility from measurements of T_g. Therefore, the laser light-scattering technique was employed to study the phase behaviour of the blends. Additionally, d.s.c. measurements were carried out to determine the composition dependence of the glass transition temperature in the area of miscibility. The experimental results are compared with calculated values.

EXPERIMENTAL

The polymerization of SAN was carried out at 60°C in ethylbenzene under N_2 with an azobisisobutyronitrile (AIBN) concentration of $0.02\,\mathrm{mol\,l^{-1}}$. The maximum degree of conversion was about 6%. The polymer was precipitated into methanol and purified and dried as usual. *Figure 1* shows the copolymerization diagram, where the AN content of the SAN was determined by the Kjeldahl method. The molecular weights of SAN were estimated by g.p.c. using polystyrene standards. The results are listed in *Table 1*. The polymerization of PMMA ($\bar{M}_w=43\,000$; $\bar{M}_w/\bar{M}_n=1.72$), the preparation of the blends and the method of laser light scattering have been described in a previous publication[7]. A Perkin–Elmer differential scanning calorimeter, model DSC-4, was used for the T_g determinations. The sample weight was about 10 mg and the heating rate $10\,\mathrm{K\,min^{-1}}$. All samples were treated for 3 min at temperatures about 30 K above T_g before measurements were started. In the d.s.c. scan the temperature of the point of inflection was taken as the glass transition temperature.

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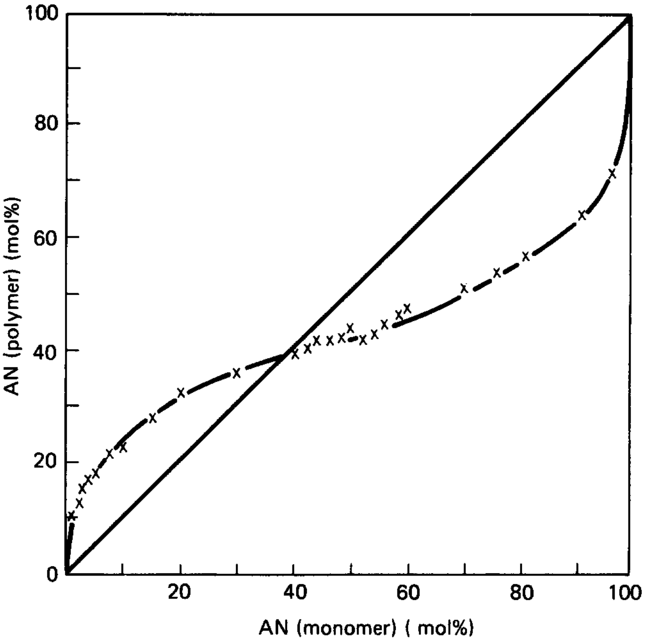

Figure 1 Copolymerization diagram of SAN at 60°C

Table 1 Molecular weight data of SAN

AN content of SAN (wt%)	$\bar{M}_w$ (g mol^{-1})	$\bar{M}_n$ (g mol^{-1})	$\bar{M}_w/\bar{M}_n$
9.4	128 000	65 000	1.97
9.8	135 000	62 000	2.18
12.9	154 000	74 000	2.08
19.2	166 000	75 000	2.21
27.0	167 000	82 000	2.04
28.2	178 000	83 000	2.14
30.5	186 000	92 000	2.02
34.4	179 000	91 000	1.97

RESULTS AND DISCUSSION

As described previously[7] the light-scattering intensity starts to increase at a certain temperature T_A. This temperature reflects an onset temperature of phase separation in the blend and varies with the heating rate. The extrapolation of the linear relationship between T_A and heating rate to heating rate zero is assumed to correspond to the binodal temperature.

The binodals thus estimated are summarized in *Figures 2* and *3* for blends containing SAN copolymers with varying AN content. It is interesting to note that in the region of low AN contents (9.4 and 9.8 wt%) the phase behaviour depends on the copolymer composition. Small changes of the SAN composition shift the phase behaviour from immiscibility to *LCST* behaviour and miscibility. Below 9.4 wt% of AN we could not observe any miscibility; above 9.8 wt% AN obviously the *LCST* values exceed the thermal decomposition temperature of the polymers.

These results were employed to construct the miscibility window of PMMA/SAN 60/40 blends (*Figure 4*). The cloud points used are listed in *Table 2*. In *Figure 4* the hatched areas reflect the range of the copolymer composition where *LCST* behaviour could be observed. Furthermore, *Figure 5* indicates the variation of the phase morphology with copolymer composition and temperature.

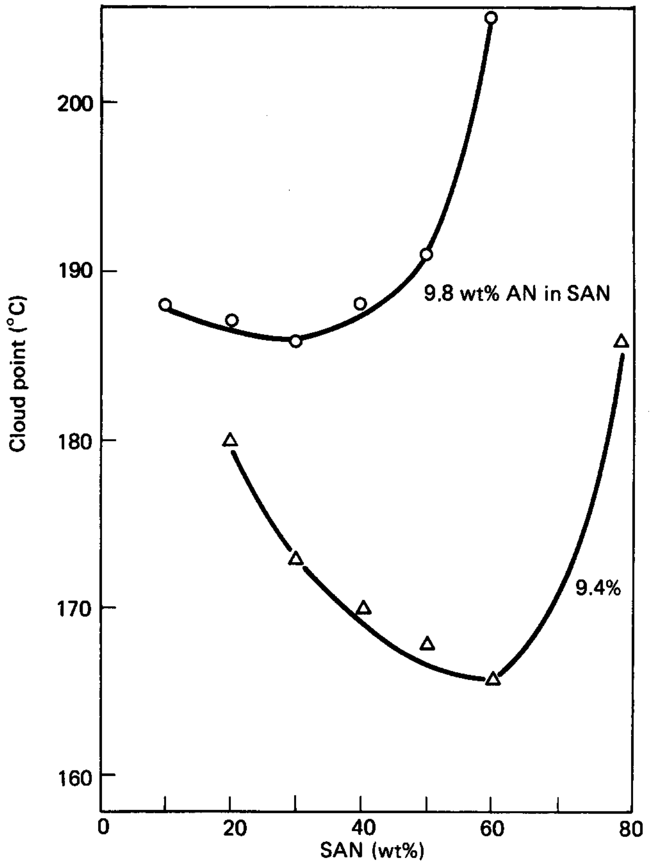

Figure 2 Binodals of SAN/PMMA blends with low AN contents in SAN

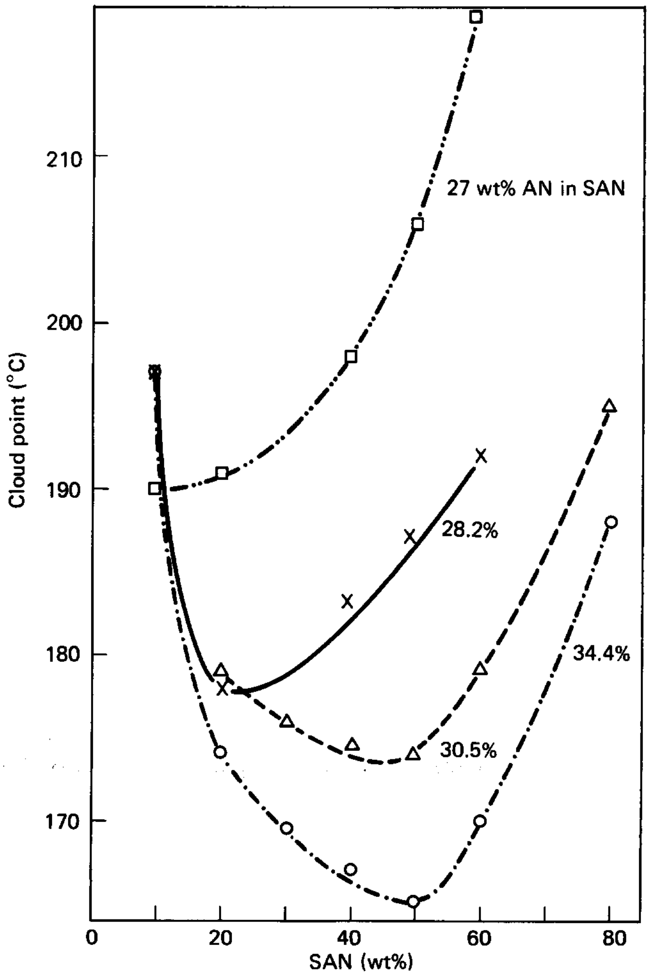

Figure 3 Binodals of SAN/PMMA blends with high AN contents in SAN

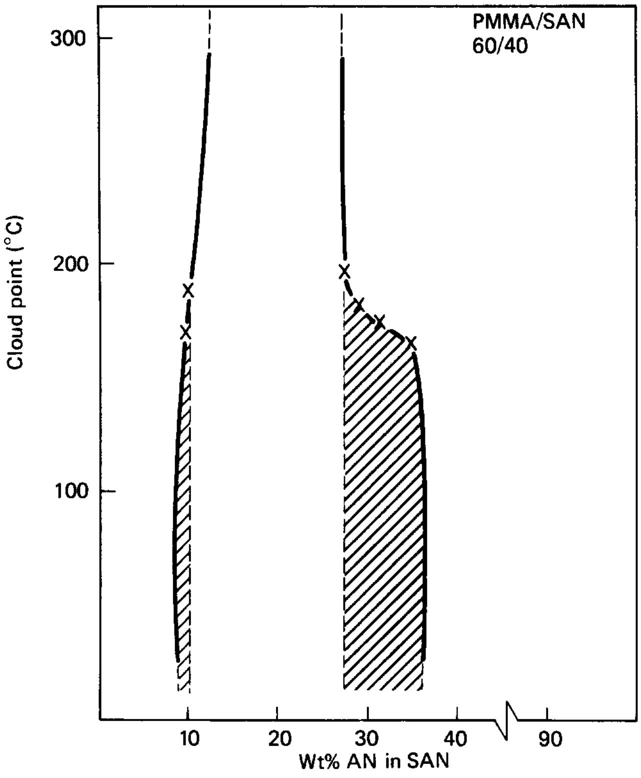

Figure 4 Miscibility window of PMMA/SAN 60/40 blends

The shape of the miscibility window here is somewhat similar to the window of PPO/P(*p*CS-*co*-*o*CS) reported elsewhere[5]. In the range of low AN content, an extremely steep descent of the cloud point occurs with decreasing AN content, whereas in the opposite limit of high AN contents the behaviour is smoother.

In an earlier paper[7] we reported that in a certain temperature range just above the *LCST* a highly interconnected two-phase morphology can be observed. It is interesting to note that the same type of morphology occurs at room temperature in a certain region of copolymer composition just outside of the window (cf. *Figure 5*).

Table 2 Cloud points used for the determination of the miscibility window

AN (wt%) in SAN	Cloud point (°C)
5.4	cloud
8.9	cloud
9.4	170
9.8	188
12.9	clear up to decomposition
26.6	clear up to decomposition
27.0	198
28.2	183
30.5	174.5
34.4	166
36.9	cloud

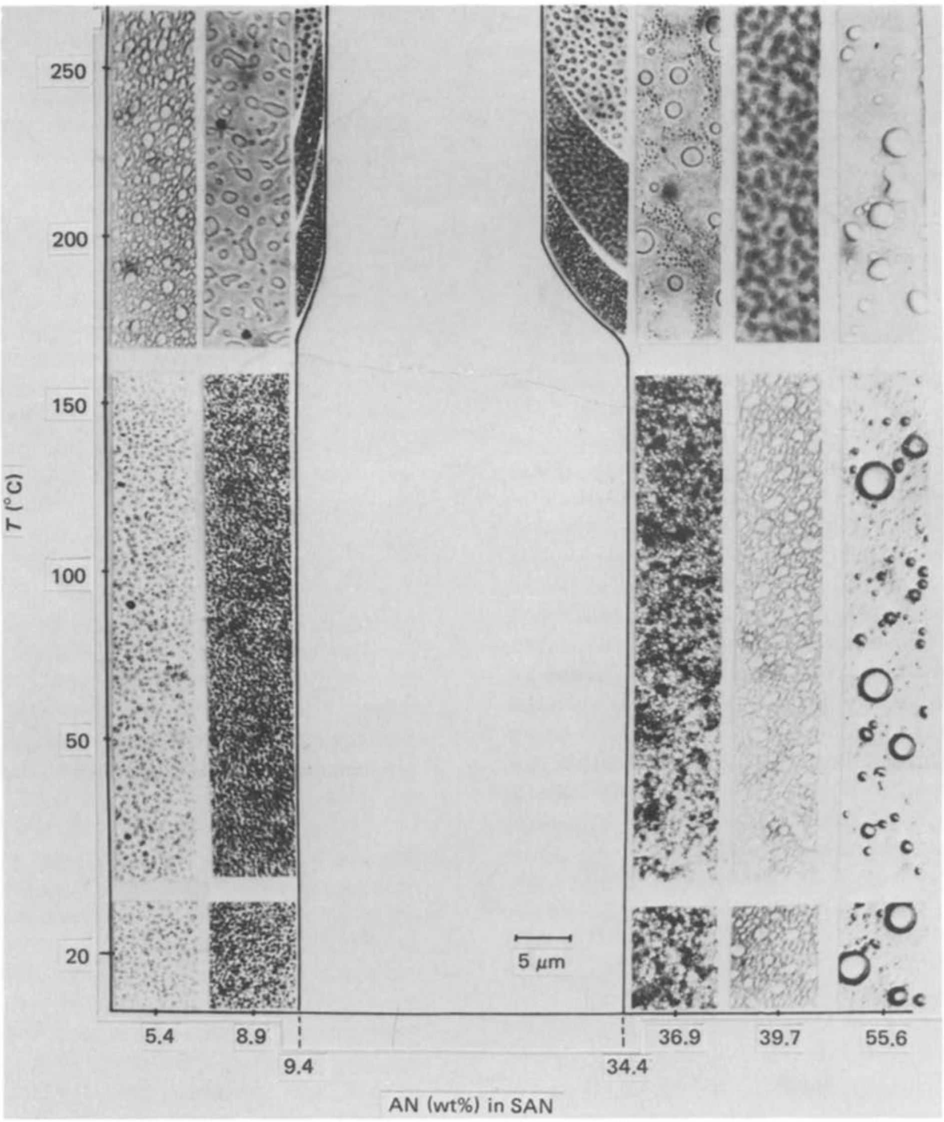

Figure 5 Variation of the phase morphology of PMMA/SAN 60/40 blends with copolymer composition and temperature

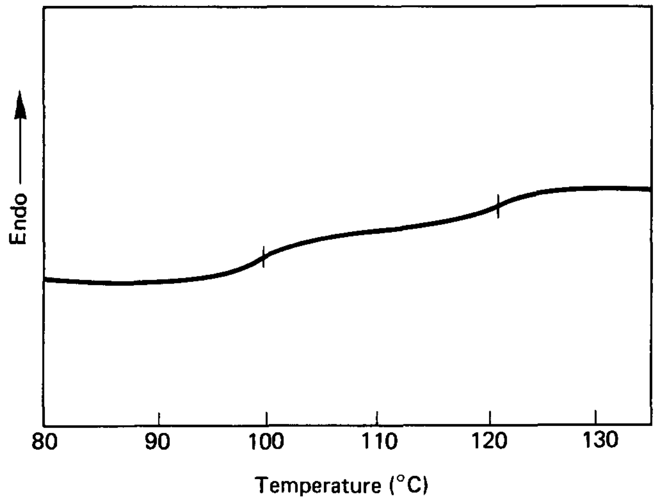

Figure 6 D.s.c. plot of a SAN/PMMA 50/50 blend containing a SAN with 5.4 wt% of AN

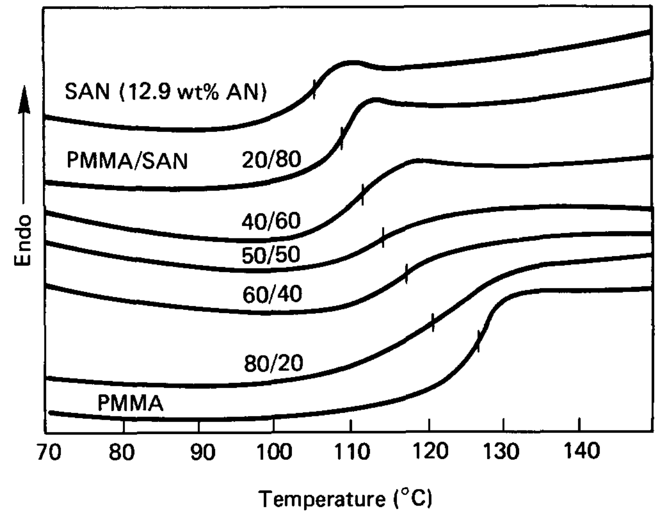

Figure 7 Composition dependence of the shape of glass transition

As mentioned above the difference in the glass transition temperatures of both components is small (in the range of 10 to 20°C). Therefore, separated glass transition temperatures could be detected only in the range of low AN contents. As an example, *Figure 6* presents a d.s.c. plot of a blend containing a SAN with 5.4 wt% of AN. Furthermore, the composition dependence of T_g was studied for three types of blends containing SAN with AN contents inside the miscibility window. *Figure 7* shows a typical example. Remarkably, a broadening of the glass transition can be observed for blend compositions above 60 wt% of PMMA. A similar response was also reported for PPO/PS blends[8]. It seems possible that the broadening of the glass transition is a general phenomenon in blends having high contents of the component with the higher glass transition temperature. The composition dependence of T_g is depicted in *Figure 8*. The Fox equation[9]:

$$1/T_g = w_A/T_{g,A} + w_B/T_{g,B} \qquad (2)$$

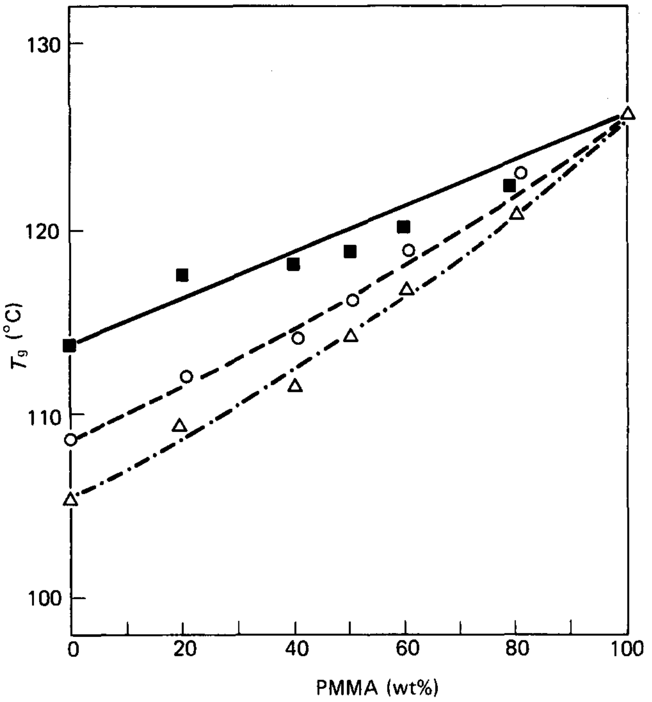

Figure 8 T_g *versus* blend composition: (△) 12.9 wt% AN in SAN; (○) 19.2 wt% AN in SAN; (■) 26.6 wt% AN in SAN

was used to calculate the curves. As can be seen, the experimental results are adequately fitted by equation (2). However, no satisfactory agreement between experimental and theoretical values could be attained by using the Gordon–Taylor equation[10]:

$$T_g = (w_A T_{g,A} + K w_B T_{g,B})/(w_A + K w_B) \qquad (3)$$

where the parameter K was estimated to be approximately 1 (ref. 11).

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