Study of the miscibility and the phase behaviour of amorphous binary blends of poly(hydroxy ether of bisphenol A) and poly(styrene-*co*-acrylonitrile)

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(Received 5 November 1992; revised 6 May 1993)

The phase behaviour of the binary polymer system consisting of poly(hydroxy ether of bisphenol A) (Phenoxy) and poly(styrene-*co*-acrylonitrile) (SAN) has been investigated by means of visual observations, light transmission measurements, differential scanning calorimetry and dynamic mechanical thermal analysis. The influence of both the blend composition and the copolymer composition of SAN on the miscibility of these binary blends was examined. All of the Phenoxy/SAN*x* ($x=5$, 10.4, 15, 16.9, 29, and 34 wt% AN) blends studied were partially miscible. The composition of the two phases and the interaction parameters were calculated from measurements based on the glass transition temperatures.

(Keywords: blend miscibility; phase behaviour; interaction parameter)

INTRODUCTION

Mixing of high-molecular-weight polymers usually results in immiscible blends as a result of unfavourable entropic contributions. It is well known that specific interactions between homopolymers can result in a negative enthalpy of mixing, therefore enhancing the miscibility[1]. In the case of homopolymer/copolymer blends (A_x/B_yC_{1-y}), the repulsion between the comonomer units in the copolymer can be responsible for the existence of a miscibility window[2–5]. The blend interaction parameter (χ_{bl}) consists of three contributions, namely two intermolecular (χ_{AB} and χ_{AC}) and one intramolecular parameter (χ_{BC}). In the absence of any specific interactions all of the χ_{ij} are positive.

$$\chi_{bl}=xy\chi_{AB}+x(1-y)\chi_{AC}-y(1-y)\chi_{BC} \qquad (1)$$

To obtain a totally miscible blend, χ_{bl} has to be smaller than a certain critical value (χ_{cr}). The molecular weight dependence of χ_{cr} is taken into account by means of the degree of polymerization of the components (x_1 and x_2).

$$\chi_{cr}=0.5(x_1^{-1/2}+x_2^{-1/2})^2 \qquad (2)$$

For high-molecular-weight polymers this critical value tends to zero. This means that the blend interaction parameter must be negative in order to satisfy the condition $\chi_{bl}<\chi_{cr}$; this can only be established when the intramolecular parameter χ_{BC} is much more positive than the intermolecular parameters χ_{AB} and χ_{AC}. This is only possible when the repulsion between the comonomer units in the copolymer is stronger than that between the monomer units of the homopolymer and copolymer.

The molecular weights of the blend components, the composition of both the blend and the copolymer, and the temperature are important parameters which all have to be taken into account in miscibility studies.

In this work, an amorphous homopolymer, poly(hydroxy ether of bisphenol A) (Phenoxy), and an amorphous copolymer, poly(styrene-*co*-acrylonitrile) (SAN), were selected and blended in various ratios. To our knowledge, this binary polymer blend system has not previously been investigated. The presence of specific interactions between both components is not obvious, but as a copolymer (i.e. SAN) is present in the blend, the copolymer (or repulsion) effect could cause miscibility. SAN is known to induce miscibility in poly(methyl methacrylate) (PMMA)/SAN homopolymer/copolymer blends[6,7] because of a strong repulsion between the styrene and acrylonitrile comonomers, and also in copolymer/copolymer blends such as SAN/poly(styrene-*co*-maleic anhydride) (SMA)[5,8,9] and others[5,10,11]. For these reasons the influence of the acrylonitrile (AN) content of the SAN copolymer on the miscibility of the Phenoxy/SAN blend was investigated in this present work.

EXPERIMENTAL

Binary blends of poly(hydroxy ether of bisphenol A) (Phenoxy) and poly(styrene-*co*-acrylonitrile) (SAN) with different copolymer compositions (i.e. 5, 10.4, 15, 16.9, 29, and 34 wt% acrylonitrile) were prepared from THF solutions (3% wt/vol), followed by coprecipitation by the addition of excess hexane. The blends obtained by this method were dried *in vacuo* for 3 days at 60°C. Several different Phenoxy/SAN compositions were prepared. The Phenoxy homopolymer was obtained from EGA CHEMIE, while the SAN copolymers were kindly supplied by DOW Benelux (The Netherlands). Some

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0032-3861/94/010162-06

molecular characteristics of the materials that were used are presented in *Table 1*.

Because the two component polymers have different refractive indices, it was possible to relate visual observations and light transmission measurements to the phase behaviour of the blends. With visual observations the transparency of the blend is investigated; a transparent blend is considered as miscible, while a cloudy blend is regarded as being partially miscible or immiscible. In light transmission experiments a light beam passes through the sample, which is heated on a hot stage (Mettler FP82) at a rate of 3°C min^{-1}, and using an optical microscope, the evolution of the light intensity (after magnification of the image ($\times 25$)) is recorded with a CCD camera. Smaller domains in the samples can be detected with this technique, when compared to visual observations. Phase separation as a function of temperature, such as lower critical solution temperature (*LCST*) phase behaviour, leads to a decrease in the transmitted light intensity.

Glass transition measurements were carried out by using either a Perkin-Elmer DSC-7 at a scanning rate of 20°C min^{-1}, or a Polymer Laboratories DMTA MKII at a scanning rate of 3°C min^{-1} and a frequency of 1 Hz. D.s.c. scans were performed on 10 mg of material. A second run was carried out in order to prevent enthalpy relaxation peaks, the presence of which makes accurate determination of the T_g difficult. This enthalpy relaxation behaviour becomes more pronounced as the SAN content in the blend is increased. Specimens (1 × 10 × 55 mm) for the dynamic mechanical thermal analysis (d.m.t.a.) studies were prepared by compression moulding at 160°C for 10 min. The values of the glass transition temperatures were estimated from the temperature of half height of inflection of the heat capacity *versus* temperature curve, and from the maximum $\tan\delta$ values in the d.s.c. and d.m.t.a. scans, respectively. Blend miscibility was monitored by using the criterion that miscible blends exhibit one T_g value, whereas phase separated blends show two glass transition points.

Scanning electron microscopy (SEM) studies were made on blends which contained only a small amount of one of the components, using the same sample preparation technique that was used for the d.m.t.a. measurements. The specimens were broken in liquid nitrogen in order to achieve a brittle fracture without any plastic deformation. This fracture surface was then coated with gold and examined with a Philips 500 scanning electron microscope.

RESULTS AND DISCUSSION

Blend miscibility behaviour

In the first type of experiments the transparency of the Phenoxy/SANx (x = 5, 10.4, 15, 16.9, 29, and 34 wt% AN) blends was examined at various temperatures between 160 and 300°C by means of visual observations. All of the blends appeared cloudy, with the exception of the (90/10), (80/20), (20/80), and (10/90) systems. This could be due to the fact that these binary combinations are either really miscible, or in the case of phase separated blends, that the sizes of both phases are smaller than the wavelength of light.

Data obtained from light transmission measurements, over the temperature range 160–300°C, showed for some of the blend compositions an initial decrease in light intensity with increasing temperature, which was followed by a constant intensity value (*Figure 1*), while for the other compositions the intensity showed almost no variation as a function of temperature (*Figure 2*). The increase in the light intensity at the end of the measurements is probably due to flow of the specimen during heating. The former behaviour was observed for the blends containing a low concentration (10% by weight) of one of the components; this can be explained by phase separation occurring at the start of the experiment, which is then followed by a stabilization of the transmitted light intensity when this process is completed. In the latter case, the phase behaviour is independent of temperature, but these measurements do not provide any information about the type of miscibility;

Table 1 Molecular characteristics of the Phenoxy homopolymer and the SANx copolymers

Material	M_w[a]	M_n[a]	M_w/M_n[a]	T_g[b] (K)
Phenoxy	45 000	18 000	2.60	362.2
SAN5	149 000	71 000	2.11	384.9
SAN10.4	123 000	59 000	2.09	381.4
SAN15	124 000	65 000	1.91	386.3
SAN16.9	185 000	63 000	2.94	381.7
SAN29	94 000	48 000	1.96	382.3
SAN34	96 000	50 000	1.92	385.1

[a] Determined by g.p.c. in THF at room temperature, using polystyrene standards

[b] Measured by d.s.c. using a scanning rate of 20°C min^{-1}

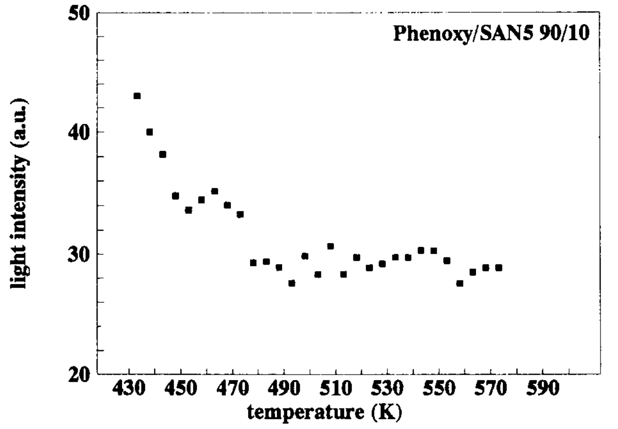

Figure 1 Light transmission measurements, carried out as a function of temperature, on the Phenoxy/SAN5 (90/10) blend

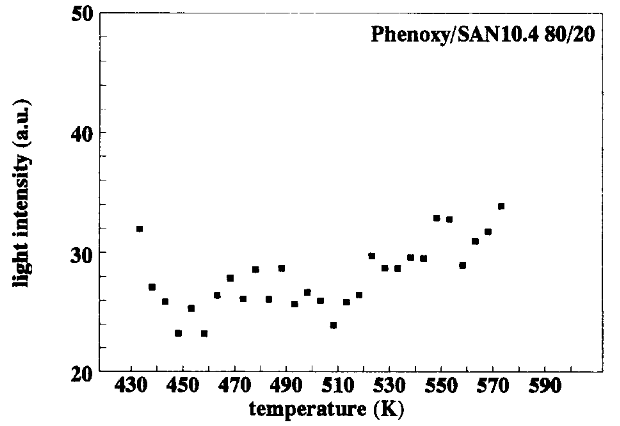

Figure 2 Light transmission measurements, carried out as a function of temperature, on the Phenoxy/SAN10.4 (80/20) blend

a miscible, as well as an already phase separated blend, will show no change in light intensity.

Differential scanning calorimetry (d.s.c.) measurements of the binary Phenoxy/SANx blends reveal two glass transition temperatures. The lower T_g, which corresponds to the Phenoxy-rich phase, increases with an increasing SAN content, while the variation of the T_g of the SAN-rich phase is less pronounced, and in the case of blends containing a SAN copolymer with a high AN content, is almost absent. This indicates that an almost pure SAN phase, as well as a mixed Phenoxy/SAN phase (i.e. a Phenoxy-rich phase), are formed. Most of the blends in which one of the components is present in a minor concentration (e.g. 10/90 and 90/10) show only one T_g. However, for the Phenoxy/SAN34 (10/90) and (90/10) blends, a second, smaller T_g can be observed. *Figures 3* and *4* show some typical d.s.c. thermograms, which were obtained for the partially miscible Phenoxy/SAN blends containing, respectively, 10.4 and 34 wt% AN.

The corresponding tan δ *versus* temperature curves for Phenoxy/SAN10.4 and Phenoxy/SAN34, obtained from d.m.t.a. studies, are presented in *Figures 5* and *6*, respectively. Again, two glass transition temperatures are observed, at values intermediate to those of the pure components, which is a characteristic feature of partially miscible blends. The lower T_g decreases monotonically, whereas the higher T_g only decreases slightly with increasing Phenoxy concentration in the case of the Phenoxy/SAN10.4 blends (see *Figures 3* and *5*). In blends with an acrylonitrile-rich SAN copolymer, at least 50 wt% Phenoxy is necessary to establish a shift of the high temperature tan δ peak which corresponds to the SAN-rich phase (see *Figure 6*). Data obtained for the (90/10) and (10/90) Phenoxy/SANx blends show only one T_g. This is also the case for the Phenoxy/SAN34 (90/10) and (10/90) blends, in contrast to the d.s.c. results, and is probably due to the broadness of the tan δ peaks, which could easily hide a smaller peak.

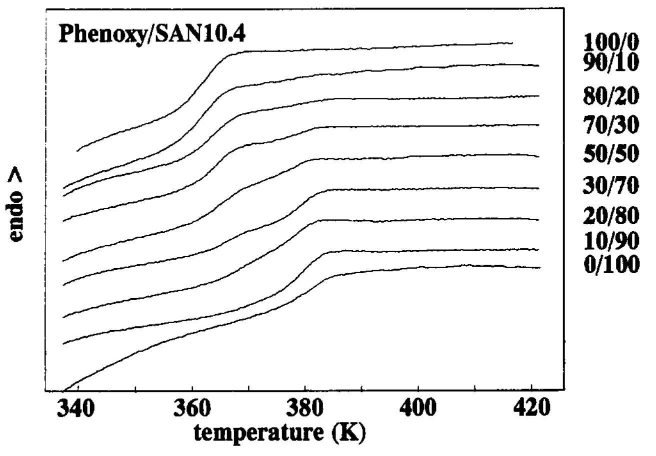

Figure 3 D.s.c. thermograms obtained for the Phenoxy/SAN10.4 blend system

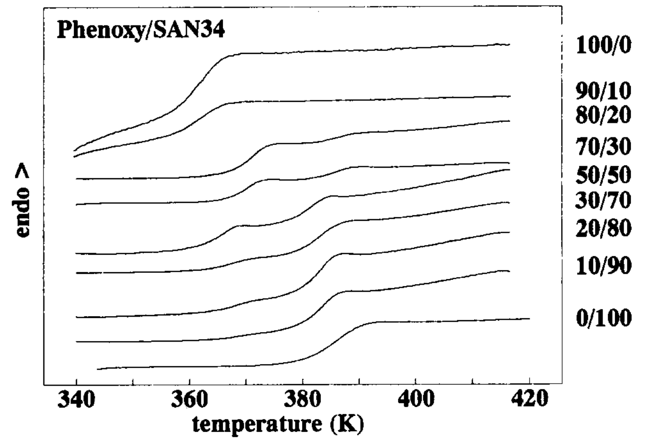

Figure 4 D.s.c. thermograms obtained for the Phenoxy/SAN34 blend system

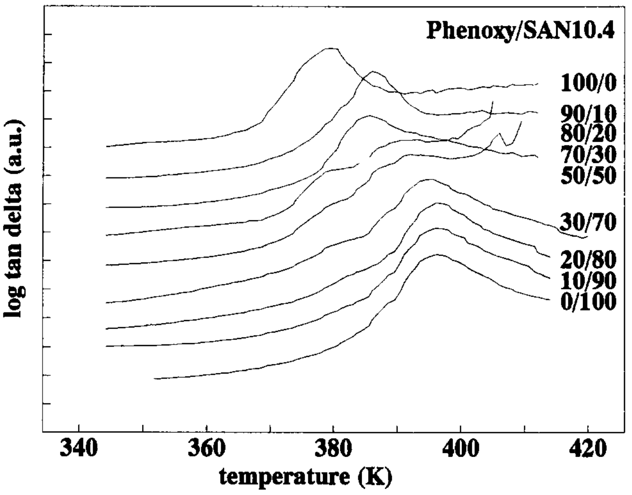

Figure 5 Tan δ *versus* temperature curves of the Phenoxy/SAN10.4 blend system obtained from d.m.t.a. measurements

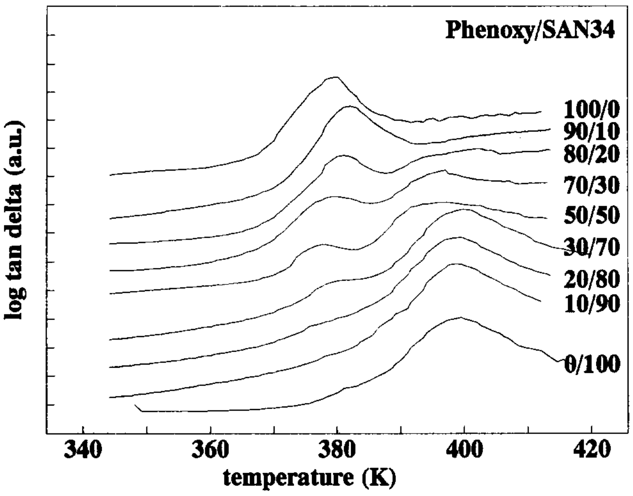

Figure 6 Tan δ *versus* temperature curves of the Phenoxy/SAN34 blend system obtained from d.m.t.a. measurements

Examination of these blends by means of scanning electron microscopy demonstrates the existence of a two-phase system (see *Figure 7*); in this micrograph a morphology consisting of a spherical phase dispersed in a matrix can be observed for the case of a Phenoxy/SAN34 (10/90) blend.

Composition of the phases in partially miscible Phenoxy/SAN blends

Glass transition temperature measurements allow us to calculate the composition of the two phases in a partially miscible blend[12,13]. This can be achieved by using the Fox relationship[14]:

$$1/T_{g_{bl}} = w_1/T_{g_1} + w_2/T_{g_2} \tag{3}$$

where $T_{g_{bl}}$ is the observed T_g of the blend, and w_i is the weight fraction of component i, which exhibits a glass transition temperature, T_{g_i}. This can be transformed into:

$$w'_1 = [T_{g_1}(T_{g_{1,bl}} - T_{g_2})]/[T_{g_{1,bl}}(T_{g_1} - T_{g_2})] \tag{4}$$

where w'_1 is the weight fraction of component 1 in the component-1-rich phase, and $T_{g_{1,bl}}$ is the observed T_g of the component-1-rich phase.

In this way the weight fraction of component 1 in both the component-1-rich phase (w'_1) and the component-2-rich phase (w''_1) can be calculated. The results for the Phenoxy/SAN10.4 blend system, calculated using the Fox relationship, are presented in *Table 2*. When both glass transition temperatures are very close to each other, it is sometimes difficult to determine them accurately. Hence, a second method has been used by taking the derivative of the original d.s.c. scans; the transitions are then translated into peaks from which the maximum is determined. Small differences are obtained for the compositions of the two phases when using these two methods (half height and maximum of the derivative). For blends which contain a SAN copolymer with a high AN content, the SANx-rich phase consists of almost pure SAN; only 3–7 wt% Phenoxy is dissolved (w''_1 is almost zero; see also *Figure 8* below). Up to 20 wt% Phenoxy is present in the SAN-rich phase for blends containing SAN with a low AN content. On the other hand, SAN dissolves up to levels of 50 wt% in the Phenoxy phase ($w'_2 = 1 - w'_1 \approx 50$ wt%, for SAN-rich blends).

The influence of the AN content of the SAN copolymer on the composition of the phases is presented in *Figure 8*. An increase in the AN content of SAN leads to a decrease of the weight fraction of Phenoxy in the SAN-rich phase (i.e. w''_1 decreases with increasing x). However, no obvious trend can be observed concerning

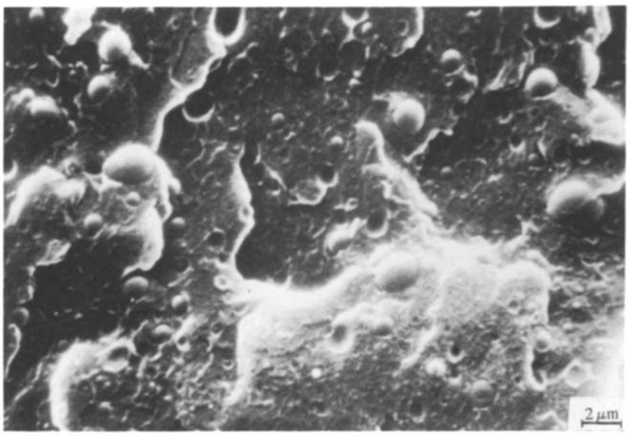

Figure 7 Scanning electron micrograph of a Phenoxy/SAN34 (10/90) blend sample

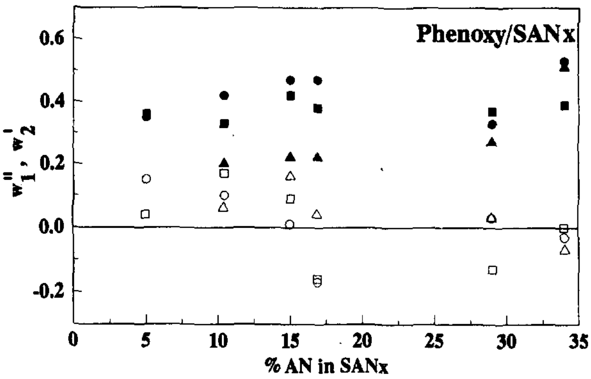

Figure 8 Influence of the acrylonitrile content on the composition of the two phases of Phenoxy/SANx blends: open symbols, w''_1; filled symbols, w'_2; circles, (20/80); squares (50/50) and triangles (80/20)

Table 2 Composition of the two phases of the partially miscible Phenoxy/SAN10.4 blend calculated by using the Fox relationship[14]

Weight fraction of SAN10.4	$T_{g1,bl}$ (K)	$T_{g2,bl}$ (K)	w'_1 ($\times 10^3$)	w'_2 ($\times 10^3$)	w''_1 ($\times 10^3$)	w''_2 ($\times 10^3$)
Method 1: using the original d.s.c. scans; T_g is the half height of the transition						
1.00		381.4				
0.90		379.7				
0.80	368.2	378.3	676±9	324±9	163±9	873±9
0.70	367.0	380.5	740±9	260±9	47±9	953±9
0.50	364.9	378.4	853±10	147±10	157±9	843±9
0.30	364.1	380.3	896±10	104±10	57±9	943±9
0.20	363.0	379.8	956±10	44±10	84±9	916±9
0.10	361.7					
0.00	362.2					
Method 2: using the derivative of the original d.s.c. scans; T_g is the maximum of the peak						
1.00		383.9				
0.90	372.0	382.3	542±8	458±8	75±8	925±8
0.80	371.1	381.8	584±8	416±8	99±8	901±8
0.70	369.1	382.0	679±9	321±9	89±8	911±8
0.50	396.2	380.3	674±9	326±9	170±8	830±8
0.30	367.2	382.6	770±9	230±9	61±8	939±8
0.20	366.7	382.6	795±9	205±9	61±8	939±8
0.10	364.3					
0.00	362.5					

the amount of SAN that dissolves in the Phenoxy-rich phase (i.e. w'_2) when the AN content is varied.

Interaction parameter calculations

Starting from the Gibbs free energy of mixing for a polymer system at equilibrium, G, which is given by the Flory–Huggins theory[15], the chemical potential can be derived:

$$\partial\Delta G/\partial n_1=\Delta\mu_1=RT[\ln\Phi_1+(1-m_1/m_2)\Phi_2+m_1\chi_{12}\Phi_2^2] \tag{5}$$

and

$$\partial\Delta G/\partial n_2=\Delta\mu_2=RT[\ln\Phi_2+(1-m_2/m_1)\Phi_1+m_2\chi_{12}\Phi_1^2] \tag{6}$$

where n_i is the number of moles of the ith component in the blend, and Φ_1 and Φ_2 are the volume fractions in the blends of Phenoxy and SANx, respectively, which are obtained by dividing the weight fractions by the densities[16]; the densities were calculated by means of the group contribution method[16]. In the above, m_1 and m_2 represent the chain lengths of the component polymers and can be obtained from the following equation:

$$m_i=M_iv_i/v_1 \tag{7}$$

where M_i is the molecular weight of polymer i, v_i is the specific volume of polymer i ($=1/d_i$, where d_i is the density), and v_1 is the molar volume of a lattice site ($=M_j/d_j$, where M_j is the molecular weight of monomer j; in this case, Phenoxy was chosen as the reference material).

Some authors use number-average molecular weights to calculate m_1 and m_2, when considering polydisperse polymers[12,17], while others prefer to use weight-average molecular weights when considering the miscibility of partially miscible polymers[18]. In this work, the number-average molecular weight has been used for calculations of the chain lengths of the component polymers (indicated by m_n in *Table 3*), since it was also used by Flory.

At equilibrium the chemical potential of each component is equal in both phases:

$$\Delta\mu'_1=\Delta\mu''_1 \tag{8}$$

and

$$\Delta\mu'_2=\Delta\mu''_2 \tag{9}$$

where ′ denotes the Phenoxy-rich phase and ″ denotes the SANx-rich phase.
Equation (8) therefore yields:

$$\chi_{12}=[\ln(\Phi''_1/\Phi'_1)+(1-m_1/m_2)(\Phi''_2-\Phi'_2)]/\{m_1[(\Phi'_2)^2-(\Phi''_2)^2]\} \tag{10}$$

In a similar fashion equation (9) yields:

$$\chi_{12}=[\ln(\Phi''_2/\Phi'_2)+(1-m_2/m_1)(\Phi''_1-\Phi'_1)]/\{m_2[(\Phi'_1)^2-(\Phi''_1)^2]\} \tag{11}$$

Table 3 Number-average chain lengths (m_n) of the Phenoxy homopolymer (m_1) and the SANx copolymers (m_2)

Polymer	d (g ml^{-1})	m_n
Phenoxy	1.252	187±9
SAN5	1.151	272±13
SAN10.4	1.155	271±13
SAN15	1.159	270±13
SAN16.9	1.161	270±13
SAN29	1.172	267±13
SAN34	1.177	266±13

Table 4 Values obtained for the interaction parameters of the Phenoxy/SAN10.4 blend system, calculated using equations (10) and (11) (see text for details)

Weight fraction of SAN10.4	Φ'_1 ($\times 10^3$)	Φ''_1 ($\times 10^3$)	χ_{12}[a] ($\times 10^4$)	χ_{12}[b] ($\times 10^4$)
1.00				
0.90				
0.80	565±9	92±7	141±12	113±9
0.70	661±10	83±7	140±12	108±9
0.50	657±10	159±8	115±11	102±9
0.30	756±10	56±7	153±15	108±11
0.20	781±10	56±7	153±15	109±11
0.10				
0.00				

[a] Calculated using equation (10)
[b] Calculated using equation (11)

Table 5 Comparison of the critical interaction parameter (χ_{cr}) and the blend interaction parameter (χ_{12}) for various Phenoxy/SANx (50/50) compositions

Blend	χ_{cr} ($\times 10^4$)	χ_{12} ($\times 10^4$)
Phenoxy/SAN5	62±4	115±11
Phenoxy/SAN10.4	65±4	102±9
Phenoxy/SAN15	62±4	113±10
Phenoxy/SAN16.9	63±4	154±14
Phenoxy/SAN29	68±4	144±13
Phenoxy/SAN34	66±4	121±11

In *Table 4* the interaction parameters are presented for the Phenoxy/SAN10.4 binary blend, calculated by using both equations (10) and (11). Theoretically, both equations should give the same values for each χ_{12} parameter. The complexity of the equations that are involved, plus the fact we are not taking into account that the polymers are polydisperse, as well as assuming that we are dealing with a system at equilibrium, lead to differences in the values. The fact that the concentration dependence of the interaction parameter was neglected (i.e. the equation of state theory was not used) will also give rise to a discrepancy between the theoretical and experimental values. In all cases, a positive blend interaction parameter, χ_{bl}, was observed; this was expected since the results obtained from all of the experiments led to the conclusion that all of the Phenoxy/SANx compositions (where $x=5$, 10.4, 15, 16.9, 29 and 34 wt% AN) form partially miscible blends, independent of the acrylonitrile content that was used. Because no information is actually available about the presence of specific interactions and/or copolymer repulsion effects between the various (co)monomers (χ_{AB}, χ_{AC} and χ_{BC} can still be positive or negative, see equation (1)), it is not possible to state the real reason for the partial demixing of the systems. In *Figure 9* the influence of the AN content on the interaction parameter is shown for some Phenoxy/SANx compositions. The

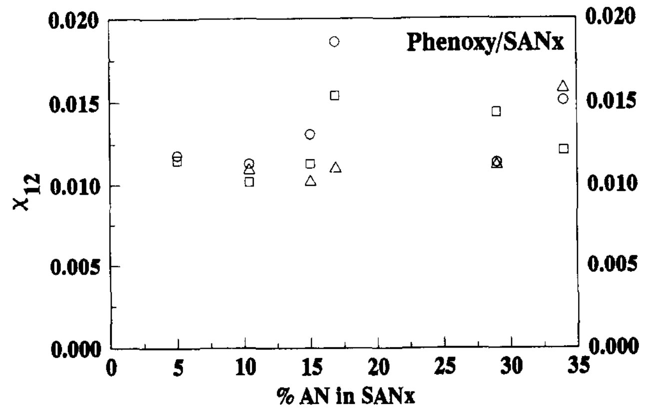

Figure 9 Influence of the acrylonitrile content on the number-average interaction parameter of some Phenoxy/SAN*x* blends: ○ (20/80); □ (50/50) and; △ (80/20)

interaction parameter of the blend seems to increase with increasing AN content. If we compare the blend χ-parameters (χ_{12}) with the critical χ-parameters (χ_{cr}), the following trend can be observed: $\chi_{12} > \chi_{cr}$ (see *Table 5*). These results are consistent with the experimental data predicting a partially miscible blend. The critical value, χ_{cr}, was calculated using equation (2), with the degree of polymerization given by $x_i = M_{i_p}/M_{i_m}$ (where M_{i_p} is the molecular weight of the polymer and M_{i_m} is the molecular weight of the monomer)[19].

CONCLUSIONS

The phase behaviour of the binary Phenoxy/SAN polymer blend system was examined by several techniques. The influence of the SAN copolymer composition on the miscibility with the Phenoxy component was investigated by using SAN with 5, 10.4, 15, 16.9, 29 and 34 wt% AN. All of the binary blends were found to be partially miscible at the temperatures studied (between room temperature and 300°C). This means that the lower critical solution temperature (*LCST*) is located at a temperature lower than ambient. By using d.s.c., a nearly pure SAN phase and a mixed Phenoxy/SAN phase were observed for the Phenoxy/SAN blends with a high acrylonitrile content. In the d.m.t.a. scans, a small shift in the value of the highest T_g is seen for all of the binary blends. By means of SEM, a morphology of dispersed spheres in a matrix is observed, even for the blends containing a small concentration of one of the components (i.e. 10 wt% SAN*x* or Phenoxy). Phase composition calculations, based on the glass transition temperatures, show that the Phenoxy component dissolves up to a level of 20 wt% in the SAN phase, while in the Phenoxy-rich phase a SAN content as high as 50% by weight can be present. For all of the Phenoxy/SAN*x* binary blends a positive interaction parameter is observed, which appears to increase with increasing AN content. The blend interaction parameter is larger than the critical interaction parameter, which is indicative for a demixed polymer system.

ACKNOWLEDGEMENTS

The authors are indebted to the IWONL for the grant offered to M. Vanneste, and to the Belgian National Science Foundation for financial support given to the Macromolecular Structural Chemistry Laboratory.

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