

# Effect of acrylonitrile content on the toughness of ABS materials

Hyungsu Kim, H. Keskkula and D. R. Paul\*

Department of Chemical Engineering and the Center for Polymer Research,  
The University of Texas at Austin, Austin, TX 78712, USA  
(Received 4 May 1990; accepted 13 June 1990)

Styrene/acrylonitrile (SAN) copolymers were toughened by addition of several SAN emulsion grafted rubbers. The main variables of the study included the AN content of the SAN graft (14.2–37.5%) and the AN content of the SAN matrix (14.7–40%). The aim was to develop general principles underlying the properties of rubber toughened SAN or ABS materials. Rubber–matrix adhesion, state of rubber particle dispersion and the inherent ductility of matrix polymer were evaluated, and the trends found in the mechanical behaviour of the blends are reasonably well explained by these three factors. The concept of inherent ductility, in particular, is effectively utilized and its importance in the ultimate properties of rubber toughened SAN is emphasized.

(Keywords: styrene–acrylonitrile copolymers; ABS; toughness; adhesion; particle dispersion; inherent ductility)

## INTRODUCTION

ABS is a family of thermoplastics that contains three monomeric units; acrylonitrile, butadiene, and styrene. Typically, a styrene/acrylonitrile copolymer (SAN) matrix contains discrete butadiene-based elastomer particles for toughening. Elastomer particles are grafted with SAN to achieve necessary interaction with the matrix polymer. In a previous paper<sup>1</sup> we described the toughening of a series of SAN copolymers by an SAN grafted butadiene rubber. The major focus was to relate the effect of acrylonitrile (AN) content of SAN matrix copolymers to blend toughness for a fixed AN composition (22.5%) of SAN graft. It was found that the maximum impact strength was obtained at mismatched AN compositions (about 34% in the matrix *versus* 22.5% in the graft) rather than when the two AN levels were equal which presumably would maximize the possibility of interpenetration of graft and matrix SAN chains.

At this composition difference of 11.5% AN, the two types of SAN chains are not expected to be fully miscible with each other because there is experimental evidence that an AN difference of more than 5% (for  $M_n \approx 10^5$ ) causes segregation between the chains<sup>2</sup>. An attempt was made to explain such behaviour in terms of three factors that affect the ductility of the blend: the rubber–matrix adhesion, the state of rubber particle dispersion and the inherent ductility of the matrix polymers.

Because of the importance of these variables in rubber toughening of brittle polymers, e.g. styrenic polymers, this type of investigation has been extended to include several well characterized SAN grafted rubbers of various AN compositions, whereas the previous work was limited to a single graft rubber. By varying only the graft AN level, we can keep the inherent ductility of the matrix fixed while affecting only issues related to interfacial adhesion and dispersion.

By keeping the difference in AN levels of the graft and the matrix constant, on the other hand, we can vary the inherent ductility while keeping the adhesion and dispersion factors relatively the same. Thus, within a wide range of AN compositions for both graft and matrix phases, it is expected that we may be able to establish an improved picture of the factors that influence the properties of rubber toughened SAN copolymers. Changes in blend mechanical properties, deformation behaviour and interfacial adhesion between grafted rubber and matrix were investigated for a number of matrix and graft compositions. Dynamic mechanical analysis was used to evaluate the intensity of the rubber phase damping peak as the interaction between the graft and matrix phase varied.

## EXPERIMENTAL

### Materials and blend preparation

The SAN grafted rubbers (SAN-g) used in this study were supplied by Asahi Chemical Industry Co. and are described in *Table 1*. A crosslinked butadiene copolymer seed latex was used for grafting with styrene/acrylonitrile monomers in a second stage of emulsion polymerization. The particles range in size from 0.1–0.3  $\mu\text{m}$ . They were characterized by extracting the soluble portion of SAN with methyl ethyl ketone (MEK). Because the butadiene rubber and the chemically bound, or grafted, SAN are not soluble in MEK (gel fraction), only the ungrafted SAN comprises the sol fraction. Knowing the gel fraction and the rubber percent from the recipe variables, the graft to rubber ratio is readily obtained as shown in *Table 1*. Typical graft rubber particle size is shown later in *Figure 8*. The glassy matrix polymers used in this study are summarized in *Table 2*.

Blends were prepared by melt mixing in a one-inch Killion extruder ( $L/D = 30$ ) using a high shear mixing screw with a compression ratio of 3 to 1. The extruded pellets were compression moulded into 3.17 mm thick

\* To whom correspondence should be addressed

**Table 1** Impact modifiers used in this study

Designation <sup>a</sup>	Rubber (%)	Graft ratio <sup>b</sup>
SAN-g-14.2	49.1	0.323
SAN-g-16.9	49.1	0.351
SAN-g-19.1	49.0	0.391
SAN-g-22.0	48.8	0.434
SAN-g-27.2	65.0	0.318
SAN-g-28.8	48.8	0.458
SAN-g-31.4	54.1	0.412
SAN-g-32.4	48.7	0.493
SAN-g-37.5	49.0	0.475

<sup>a</sup>Numbers in the abbreviation indicate per cent AN in free SAN<sup>b</sup>(Gel%-Rubber%)/Rubber%**Table 2** Matrix polymers used in this study

% AN	Abbrevia- tion	Designation	Molecular weight
0	PS	Styron 685D <sup>a</sup>	$\overline{M}_w = 300\ 000$ $\overline{M}_n = 132\ 000$
6.3	SAN 6.3	Experimental polymer <sup>a</sup>	$\overline{M}_w = 343\ 000$ $\overline{M}_n = 121\ 000$
14.7	SAN 14.7	Experimental polymer <sup>b</sup>	$\overline{M}_w = 182\ 000$ $\overline{M}_n = 83\ 000$
20	SAN 20	XP 72006 <sup>a</sup>	$\overline{M}_w = 178\ 000$ $\overline{M}_n = 88\ 000$
25	SAN 25	Tyrl 1000 <sup>a</sup>	$\overline{M}_w = 152\ 000$ $\overline{M}_n = 77\ 000$
30	SAN 30	Tyrl 880 <sup>a</sup>	$\overline{M}_w = 168\ 000$ $\overline{M}_n = 81\ 000$
33	SAN 33	Experimental polymer <sup>c</sup>	$\overline{M}_w = 146\ 000$ $\overline{M}_n = 68\ 000$
34	SAN 34	Experimental polymer <sup>b</sup>	$\overline{M}_w = 145\ 000$ $\overline{M}_n = 73\ 000$
40	SAN 40	Experimental polymer <sup>b</sup>	$\overline{M}_w = 122\ 000$ $\overline{M}_n = 61\ 000$
58	SAN 58	Experimental polymer <sup>c</sup>	<sup>d</sup>
68	SAN 68	Experimental polymer <sup>c</sup>	<sup>d</sup>

<sup>a</sup>Provided by The Dow Chemical Co.<sup>b</sup>Provided by Asahi Chemical Industry Co., Ltd<sup>c</sup>Provided by Monsanto Co.<sup>d</sup>Polymer not soluble in THF for g.p.c.

plaques. Due to the limited amount of SAN-g materials, the gross rubber content of the blends was fixed at 30% for all cases. Blends with selected SAN matrix polymers were prepared based on the AN content of SAN-g in order to reach a range of properties that would clearly distinguish major changes.

#### Material testing

Mechanical properties and deformation behaviour were assessed by the same procedures described in detail previously<sup>1,3</sup>. Interfacial adhesion between grafted rubbers and matrix polymers was determined using a lap shear method. The specimens for the test were prepared by compression moulding to form a three-piece sandwich structure having two outer layers of SAN and an inner layer of SAN-g. The SAN outer layers were approximately 6.35 mm thick while the inner layer was approximately 0.38 mm. Relatively thick plaques were used for the outer layer to preclude fracture of this layer prior to interfacial failure. The three sheets were placed together and welded in a compression mould at  $130 \pm 3^\circ\text{C}$  under pressure of 1.4 MPa for 7 min to form the bond at the

two interfaces. Then  $10.16 \times 2.03$  cm strips were cut and notched so that a lap shear joint of  $1\text{ cm}^2$  area was formed.

The dynamic mechanical measurements at 3 Hz were made in the double cantilever bending mode by using a Polymer Laboratories DMTA. The temperature was varied from  $-150$  to  $150^\circ\text{C}$  at a heating rate of  $2^\circ\text{C min}^{-1}$ . The specimen cross section was  $12 \times 3\text{ mm}^2$  with a span of 14 mm.

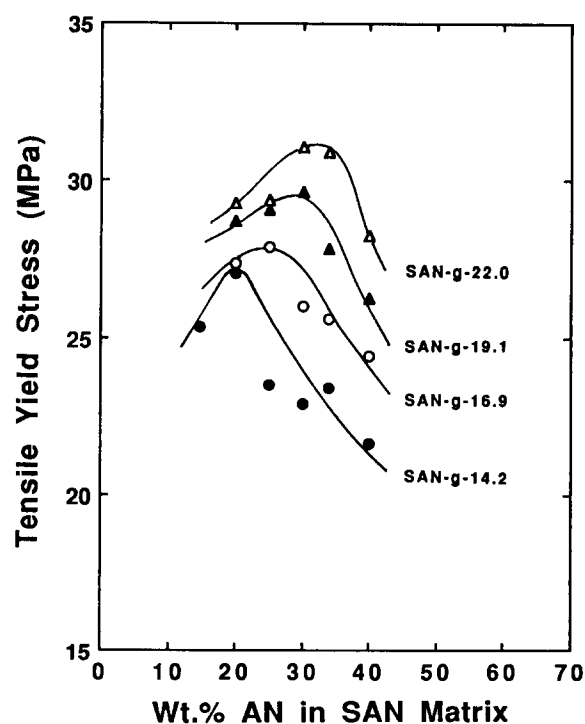
## RESULTS

### Tensile and impact properties

Figure 1 shows the tensile yield strength as a function of AN content of the matrix for blends with SAN-g materials having 14.2–22.0% AN in the graft. As stated earlier, the quantities available for the other SAN-g materials shown in Table 1 were not sufficient to make blends with all the SAN matrices included in Figure 1. It is noted that there is a maximum tensile yield strength for each SAN-g blend and that the level of the strength increases as the AN content of the graft increases.

Figure 2 shows the Young's modulus for the blends as a function of AN content in the matrix. Neither matrix composition nor graft composition has a significant effect on the modulus of these blends. The results summarized in Table 3 show that a maximum strain at failure is observed for each series. The SAN copolymer that gives maximum tensile strength and break strain coincides with that which gives the maximum Izod impact strength as seen in Figure 3.

The notched Izod impact strengths of SAN blends with SAN-g-14.2 through SAN-g-22.0 are summarized in Figure 3. In each plot, the impact strength reaches a maximum value at an AN level of the matrix that is higher than that of the graft (indicated by the arrows). Furthermore, the peak impact strength increases as the



**Figure 1** Tensile yield strength of blends (30% rubber) versus wt% AN in SAN matrix

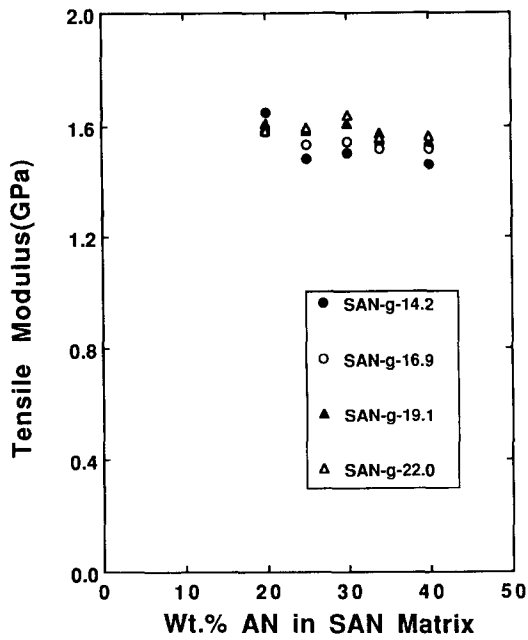


Figure 2 Tensile modulus of blends (30% rubber) versus wt% AN in SAN matrix

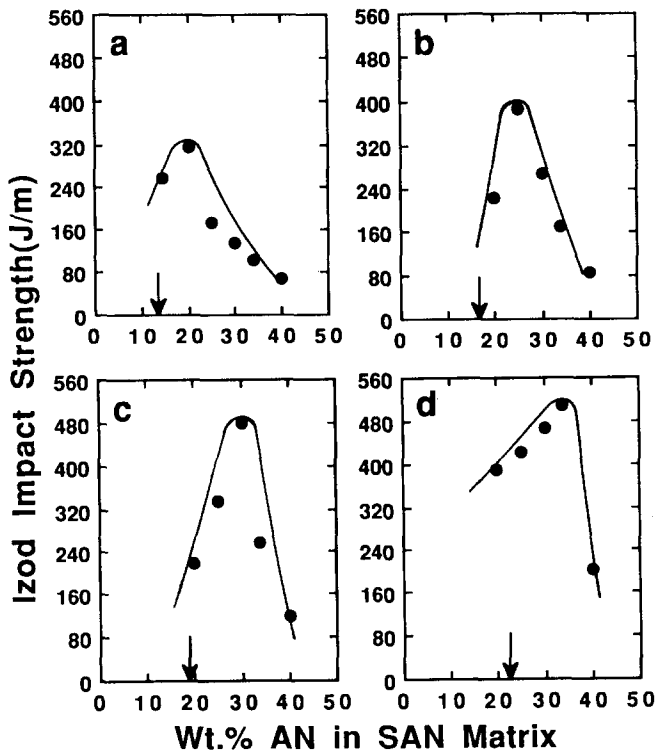


Figure 3 Notched Izod impact strength of blends (30% rubber) versus wt% AN in SAN matrices: (a) SAN-g-14.2; (b) SAN-g-16.9; (c) SAN-g-19.1; (d) SAN-g-22.0

Table 3 Break strain (%) of the blends as a function of AN content in the matrix SAN at 30% rubber

% AN	SAN-g-14.2	SAN-g-16.9	SAN-g-19.1	SAN-g-22.0
14.7	5.1	—	—	—
20	9.8 <sup>a</sup>	5.2	6.1	6.3
25	3.9	8.7 <sup>a</sup>	8.1	5.3
30	4.0	4.8	10.8 <sup>a</sup>	5.6
34	3.1	4.4	7.8	9.6 <sup>a</sup>
40	2.3	2.9	5.8	8.9

<sup>a</sup>Numbers indicate the maximum value of break strain for each series of blend. The AN contents at maxima correspond to those for maximum tensile yield strength

AN content of the graft SAN increases. The results obtained earlier<sup>1</sup> for blends with a commercial SAN-g fit satisfactorily into the present picture.

Interfacial adhesion

Results from lap shear adhesion tests are shown in Figures 4 and 5. The effects of changing AN level in the matrix polymer (outer layer) and in the graft (centre layer) on the interfacial adhesion are shown respectively. Figure 4 shows lap shear adhesion results for a fixed graft material (SAN-g-16.9) as the AN content of the SAN

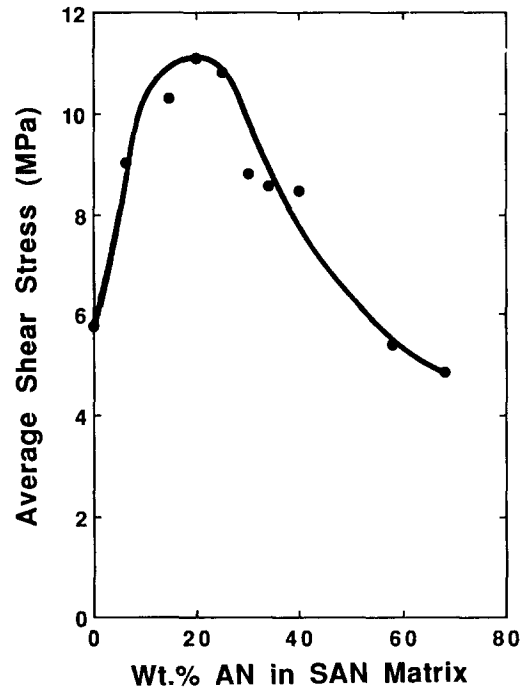


Figure 4 Average lap shear adhesive strength of joints formed from SAN-g-16.9 versus wt% AN in SAN matrix

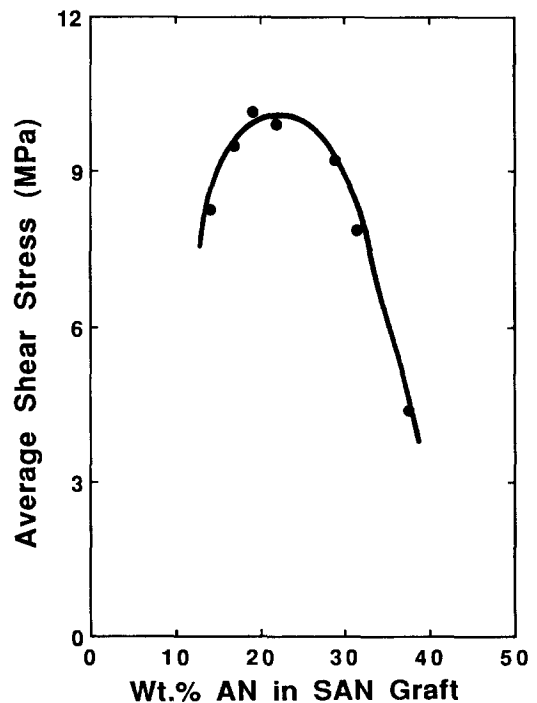


Figure 5 Average lap shear adhesive strength of joints formed from SAN 25 versus wt% AN in SAN graft

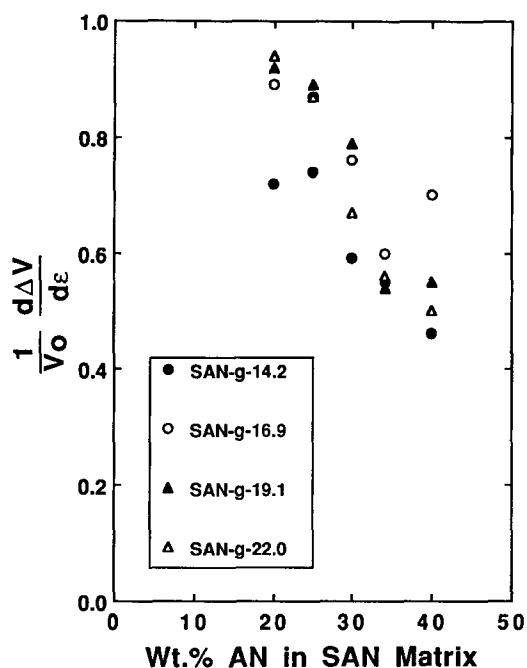


Figure 6 Slope of post-yield volume strain versus axial strain for blends at 30% rubber as a function of SAN matrix

copolymer is varied from 0 to 68%. Figure 5 represents the case of constant matrix component (SAN 25) with varied AN composition in the graft (14.2 to 37.5% AN).

In both Figures 4 and 5, broad maxima are observed around the composition where the graft and matrix compositions are matched. However, a relatively high level of adhesion persists even beyond the miscibility range of the two components.

#### Deformation behaviour

Information about the deformation behaviour of the various blends was obtained from a liquid displacement stress dilatometer described elsewhere<sup>1,3</sup>. The results are shown in Figure 6 in terms of the slope of the post-yield volume dilation versus axial strain (slope =  $(1/V_0)(dV/d\varepsilon)$ ). A slope of unity represents a purely dilatational response such as crazing while a slope of zero indicates the constant volume response of shear yielding. For mixed modes of shear deformation and dilatational processes, the slope may lie between 0 and 1. All of the blends considered here deform in a similar manner, and no significant differences result from use of different types of SAN-g.

The deformation mode primarily involves dilatational processes such as crazing or hole formation. However, increasing the AN content of the matrix results in a larger contribution from shear yielding. Similar behaviour was observed in our previous study<sup>1</sup> and by others<sup>4</sup>. The data in Figure 6, however, only reflect deformation behaviour at low test speeds. Other conclusions may be reached at different test speeds or for other types or concentrations of grafted rubber in SAN<sup>5</sup>. For instance, while polystyrene (PS) deforms by crazing in high impact polystyrene, it deforms by shear yielding when modified with a high concentration of PMMA grafted rubber<sup>6</sup>.

#### DISCUSSION

The results obtained in this work are generally consistent

with those found previously<sup>1</sup> where the impact modifier used was a commercial product of Sumitomo Naugatuck Co. There are some differences in characteristics such as particle size, size distribution and graft ratio among the experimental graft polymers used here and relative to the previously used commercial modifier. However, the main factors that affect the blend mechanical properties are believed to be the AN levels in the graft and the matrix, as emphasized previously. With this perspective, the present data are interpreted below in a rational manner that explains most of the observed results.

#### Interpretation of tensile yield behaviour

The trends shown in Figure 1 reflect the interplay between the tensile yield strength of neat SAN and the state of rubber particle dispersion in the blends. The tensile yield strength of the SAN matrix polymer monotonically increases with increasing AN content as shown in Figure 7. The degree of rubber particle dispersion is influenced by the miscibility of the graft and the matrix SAN chains. As an example of the differences in rubber particle dispersion, transmission electron micrographs of blends of SAN-g-16.9 with SAN 20 and SAN 40 are shown in Figures 8a and b, respectively.

In Figure 8a, the difference in AN content between the graft and the matrix is within the miscibility range ( $\Delta AN < 5\%$ ), while in Figure 8b it is far outside of this range<sup>2</sup>. Consequently, there is phase separation between the SAN chains in the grafted material and those in the matrix. The rubber particles reside in only one of these phases which results in a non-uniform distribution throughout the blend as may be seen in Figure 8b.

On the other hand, when the two types of SAN materials are miscible, there are no regions that exclude rubber particles. Thus, a relatively uniform dispersion is achieved as shown in Figure 8a. A similar trend in the state of rubber particle dispersion was observed previously<sup>1</sup>. Non-uniform dispersion can lead to a reduction

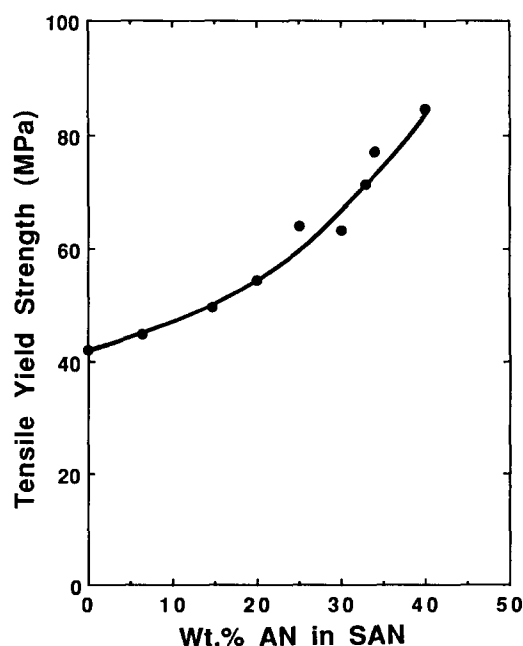
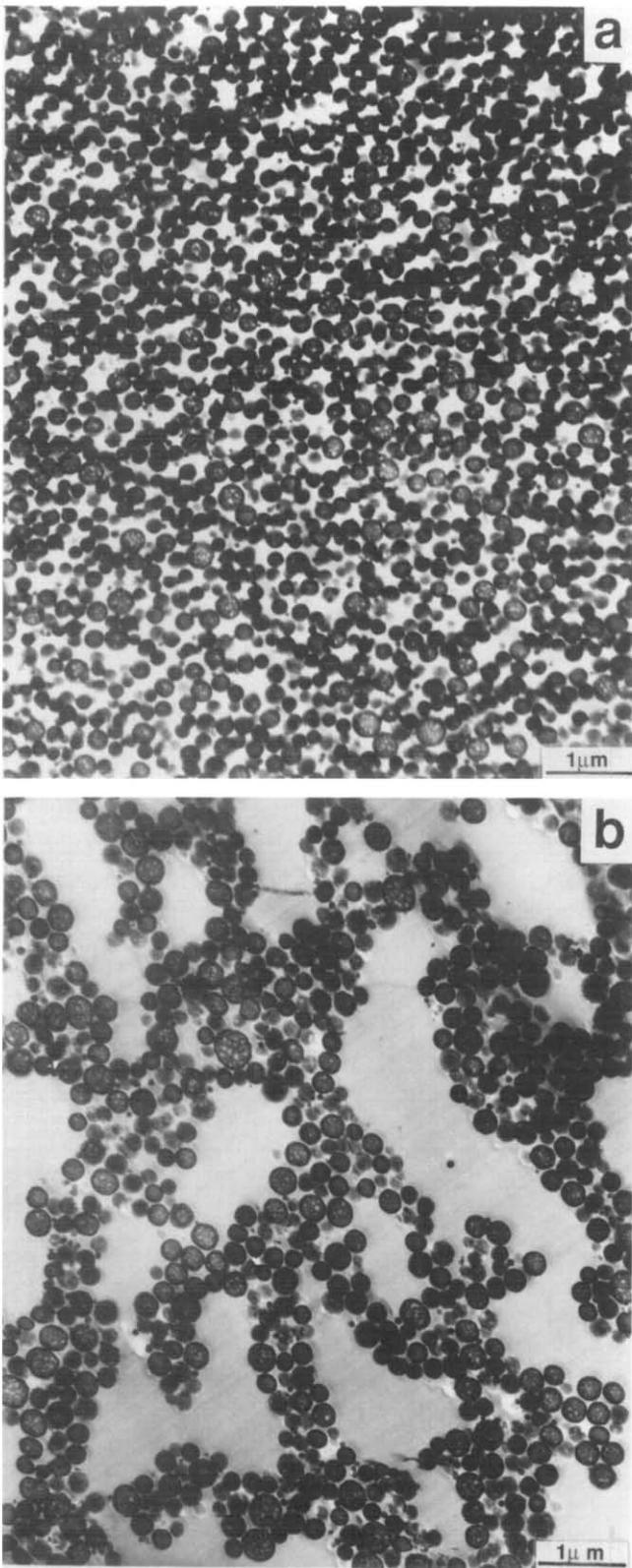


Figure 7 Tensile yield strength versus wt% AN in SAN (ref. 1)



**Figure 8** Transmission electron photomicrographs of  $\text{OsO}_4$  stained ultrathin sections for SAN-g-16.9 blends; (a) SAN 20 (3.1%); (b) SAN 40 (23.1%). Blends contain 30% rubber. Numbers in the parenthesis indicate the difference in % AN of the SAN-g-16.9 and matrix SAN

in the yield strength because of the localized regions of high rubber concentrations and/or interaction of stress fields between rubber particles as suggested by Matsuo *et al.*<sup>7</sup>. Therefore, the matrix AN content at the maximum tensile yield strength for a particular graft material reflects

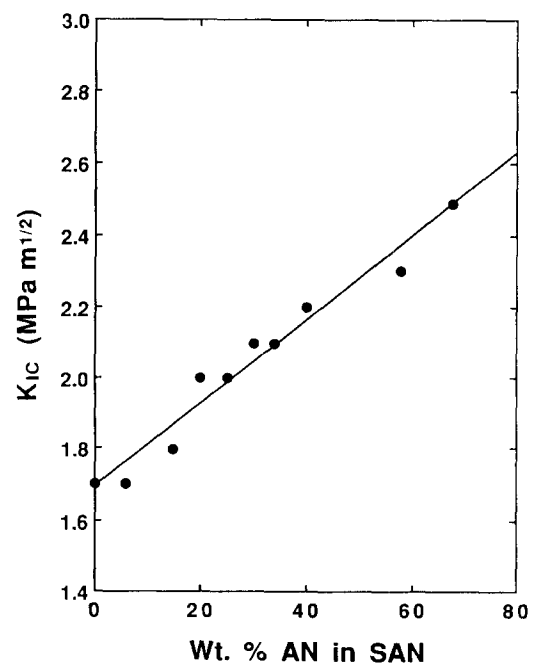
the composition at which incomplete dispersion of the rubber particles begins to overcome the increase in the strength of the matrix caused by raising its AN content.

In addition to the above reasoning, another variable that should be considered here is the interfacial adhesion between the components. Insufficient adhesion will lead to a reduced level of stress transfer for yielding across the interface between the components and consequently result in a lower yield strength. Comparison of the results shown in *Figure 1* (matrix or graft AN content fixed) with the trends shown in *Figures 4* and *5* suggests that the level of interfacial adhesion could be a factor that affects the yield strength of the blend.

#### *Factors affecting impact properties of the blends*

The fact that toughness is maximum at mismatched AN compositions requires consideration of several possible contributing factors. Stress transfer between the matrix and the grafted rubber particles is expected to be most efficient when the AN levels of the SAN chains are the same or at least within the miscibility range. Lap shear measurements described earlier indicate that there is good adhesion between types of SAN having an AN differential broader than the miscibility range centred on the AN content of the SAN graft<sup>1</sup> but the adhesion level eventually falls rapidly at higher AN difference.

The inherent ductility of the SAN matrix copolymers is another factor that influences toughenability. It was suggested previously<sup>1</sup> that this property must increase with increasing AN content. In other words, SAN copolymers with high AN levels should be more easily toughened with appropriate graft rubber particles, assuming that other factors are equal. This postulate was supported by the evaluation of the plane strain fracture toughness,  $K_{IC}$ , for a series of SAN copolymers<sup>8</sup>. The results are reproduced in *Figure 9* where a linear relationship between  $K_{IC}$  and AN content in SAN is seen. Of course, particle size and size distribution may also be important factors, but in these experiments, the rubber



**Figure 9** Plane strain fracture toughness,  $K_{IC}$  versus wt% AN in SAN (ref. 8)

particle size was substantially constant because the same seed rubber was used in all grafts.

The state of rubber particle dispersion is also expected to be a factor. In the present case, this is influenced by the miscibility between the matrix and the graft SAN chains as shown in Figures 8a and b. It is generally recognized that a significantly nonuniform structure is detrimental to effective toughening<sup>9,10</sup>.

Because of the demonstrated increase in toughenability of SAN copolymers as the AN content increases, ABS materials should generally become tougher as the matrix AN content increases provided the adhesion and dispersion issues remain within acceptable limits. The latter two are intimately connected through the difference in AN content of the matrix and the graft SANs.

As discussed above, the dispersion may become limiting before adhesion does as the difference in AN content increases. However, for the remainder of this discussion we will refer to the two collectively because we cannot distinguish their individual effects unambiguously. Figure 10a attempts to show in a diagrammatic way what happens when the graft AN level is fixed while the matrix AN level is changed. There is a reasonably wide range of matrix AN contents where adhesion or dispersion are good enough, and within this range the matrix ductility continues to increase, hence, so does

blend toughness. However, eventually the adhesion or dispersion decreases and so does blend toughness.

Figure 10b shows, in similar manner as Figure 10a, what this simple model predicts for the case when matrix AN content (thus, matrix inherent ductility) is fixed and the AN content of the graft is varied.

Figure 11 is an attempt to examine the current results in this manner. Unfortunately, not enough quantity or variety of materials were available to make this analysis fully definitive. Nevertheless, the results available reasonably support the notion that blend toughness has a broad plateau for a range of graft AN levels that encompasses that of the matrix and then falls rapidly at both higher and lower graft AN levels. This region of maximum toughness is approximately centred about the matrix AN level for SAN 30, but it seems somewhat skewed to one side for SAN 34. The expected decrease at high graft AN levels was not seen for SAN 40 simply because no grafts in this region were available. The data of Stafford and Adams shown in a recent paper<sup>11</sup> indicates a rather similar behaviour when styrene-maleic anhydride (SMA) copolymers were toughened by several SAN grafts of various AN compositions onto the same rubber seed latex for grafting. Because of the miscibility relation of SAN and SMA copolymer, similar arguments apply as discussed recently<sup>11</sup>.

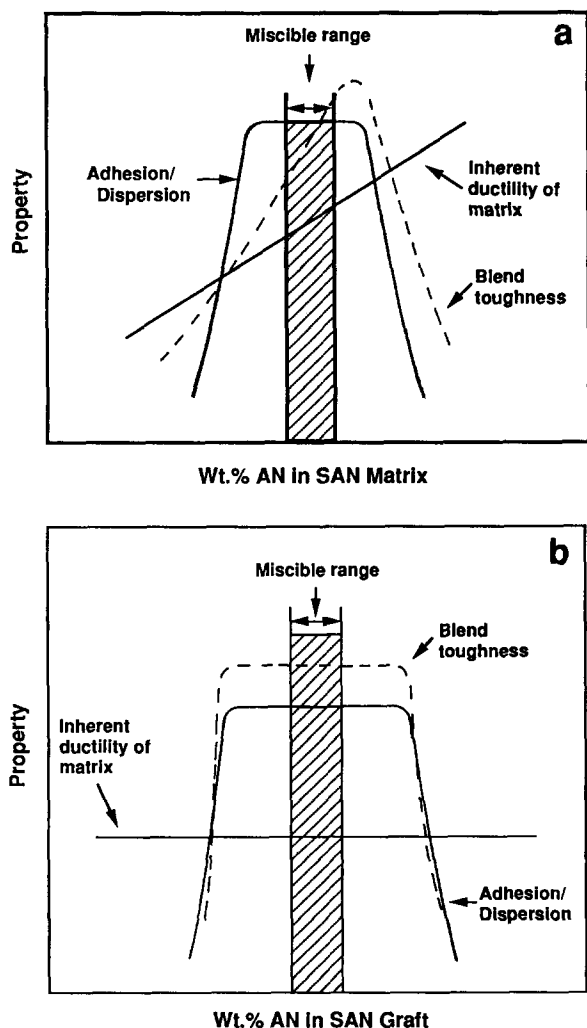


Figure 10 Schematic diagram showing the factors affecting toughness of SAN-g/SAN blends; (a) fixed graft composition; (b) fixed matrix composition

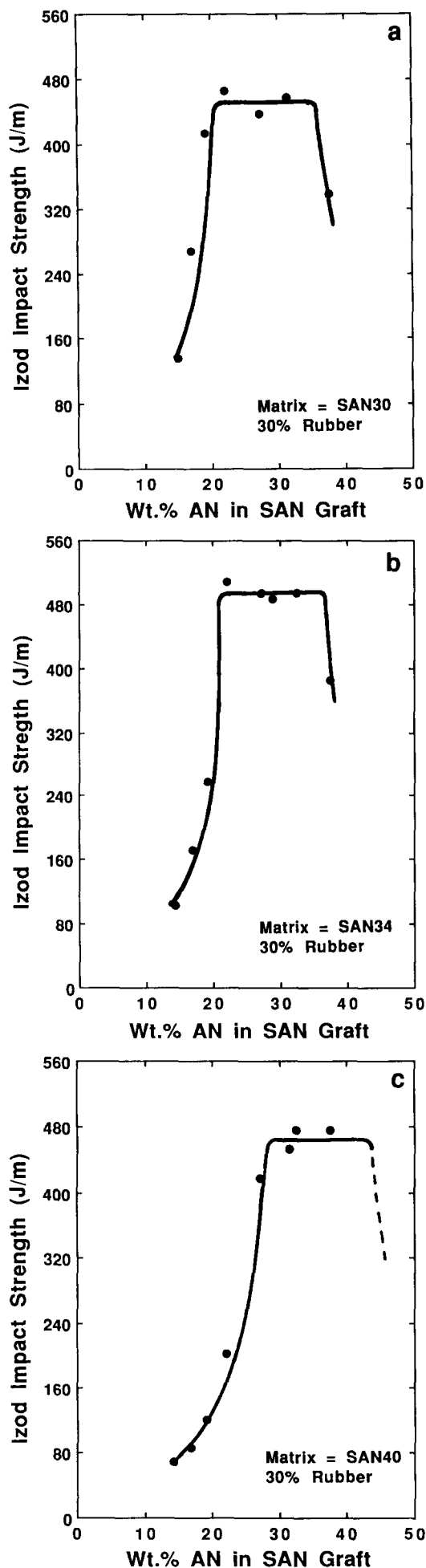
#### Dynamic mechanical properties

A number of studies of dynamic mechanical properties of ABS materials have considered the effects of seed latex and grafting variables such as particle size, dispersion and degree of grafting<sup>12-16</sup>. Most of these investigations have used ABS polymers having matched AN contents in the matrix and the graft. Masuda *et al.*<sup>17</sup>, however, varied the levels of AN in the graft (21.4 to 29.7%) and the matrix (25 to 26.4%) to study effects of rubber particle dispersion on viscoelastic properties. Here, we examine over a wider range the effect of matrix-graft interaction on the damping behaviour of the rubber phase in SAN-g/SAN blends.

Mismatch of AN content between the graft and the matrix, as emphasized earlier, affects the degree of interaction between the matrix and the dispersed rubber particles. Figure 12a and b shows the dynamic mechanical properties for the SAN-g-22 and its blend with SAN 20 as a function of temperature at 3 Hz. The storage modulus,  $E'$ , and  $\tan \delta$  curves are typical of two phase systems showing both rubber and hard matrix phase transitions. Similar results were obtained for all SAN-g blends with various matrix polymers.

Table 4 summarizes the dynamic mechanical data for SAN-g blends. Changes in the maximum height of the rubber damping peak,  $(\tan \delta)_{\text{Max}}$  and  $T_g$  of rubber phase are most probably due to some graft process variations. The AN level in the graft has little or no effect on the dynamic mechanical properties of the SAN-g. Values for  $(\tan \delta)_{\text{Max}}$  and  $T_g$  reflect the effect of graft ratio and rubber content for each SAN-g. As suggested by McCrum<sup>18-20</sup>, the height of the rubber damping peak is influenced by the quantity of rubber active in the transition region, while the  $T_g$  of the rubber phase is affected by the state of triaxial tension around the particles<sup>13</sup>.

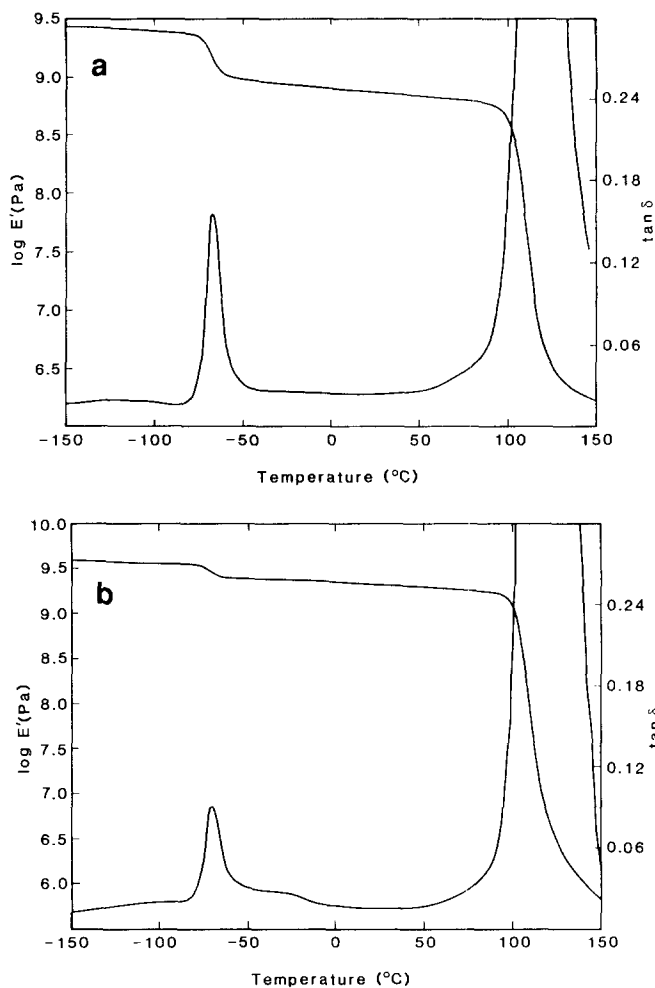
High degrees of grafting cause a stronger coupling between the rubber and the matrix. This gives rise to a higher triaxial tension in the rubber phase mainly because



**Figure 11** Notched Izod impact strength versus % AN of the SAN grafts for fixed matrix compositions at 30% rubber; (a) SAN 30; (b) SAN 34; (c) SAN 40

of the expansion mismatch and consequently the rubber experiences appreciable dilation<sup>21-24</sup>. As a result, the transition peak shifts to a lower temperature<sup>25,26</sup>. Because of these two effects, SAN-g-27.2, which has the highest rubber concentration and the lowest graft ratio among the series, has the highest  $(\tan \delta)_{\text{Max}}$  and  $T_g$ . On the other hand, most of the SAN-g blends have rather similar graft ratios and rubber contents and, thus, show little variation in  $(\tan \delta)_{\text{Max}}$  or  $T_g$ .

The glass transition temperatures of the rubber phase after blending with SAN are listed in Table 5. For every



**Figure 12** Dynamic mechanical properties of (a) SAN-g-22.0; (b) SAN-g-22.0/SAN 20 at 3 Hz

**Table 4** Summary of dynamic mechanical properties of SAN-g

Designation	$(\tan \delta)_{\text{Max}}$	$T_g$ (°C)
SAN-g-14.2	0.189	-74
SAN-g-16.9	0.191	-75
SAN-g-19.1	0.188	-75
SAN-g-22.0	0.180	-75
SAN-g-27.2	0.282	-71
SAN-g-28.8	0.174	-75
SAN-g-31.4	0.207	-73
SAN-g-32.4	0.171	-75
SAN-g-37.5	0.164	-75

graft material, the rubber phase  $T_g$  is lowered by blending with SAN. However, the amount that  $T_g$  is lowered diminishes with increasing AN content of the SAN. For SAN 40, there is essentially no difference in rubber phase  $T_g$  for the blend relative to the neat graft, whereas for SAN 20 this difference is most pronounced.

Figure 13a, b, c and d shows how  $(\tan \delta)_{\text{Max}}$  varies for blends of the grafts with different matrix compositions. In each case,  $(\tan \delta)_{\text{Max}}$  gradually increases as the AN content of the matrix increases. As stated above, the rubber phase transition temperature is lowered as the degree of grafting is increased. The degree of grafting is, of course, a constant within each series of blends. However, a similar effect on triaxial tension may be created by the degree of interaction of the matrix SAN with the grafted SAN. The data in Table 5 suggest that matching AN contents of the matrix and the graft lead to a lower rubber phase  $T_g$  in the blend than that of the neat SAN-g. There is evidence from a variety of sources suggesting that the height of this peak may also be related to the degree of adhesive coupling between the matrix and modifier phases. For example, Murayama and Lawton have shown that the dynamic energy loss in tire-cord and rubber composites is linearly correlated with the peel adhesion between the cord and the rubber<sup>27</sup>. Chua showed that the interfacial shear strength in the glass-fibre reinforced polyester correlates with the intensity of damping peak of the composite<sup>28</sup>. They concluded that dynamic mechanical analysis can be used to characterize the quality of bonding in the interfacial region. Comparison of the data in Figure 13 with the results from lap shear test (see Figures 4 and 5) leads to a similar conclusion. The decrease in lap shear strength relates to the increase in  $(\tan \delta)_{\text{Max}}$ .

SUMMARY AND CONCLUSIONS

The mechanical behaviour of blends of various SAN graft and matrix polymers has been examined. It was consistently found that blend mechanical properties are best

Table 5 Glass transition temperatures (°C) of rubber phase in SAN-g/SAN blends (30% rubber) at 3 Hz

Matrix polymer	SAN-g-14.2 (-74) <sup>a</sup>	SAN-g-16.9 (-75) <sup>a</sup>	SAN-g-19.1 (-75) <sup>a</sup>	SAN-g-22.0 (-75) <sup>a</sup>
SAN 20	-78	-78	-78	-78
SAN 25	-76	-76	-77	-77
SAN 30	-76	-76	-76	-77
SAN 34	-75	-75	-76	-76
SAN 40	-75	-74	-75	-76

<sup>a</sup>Number in the parenthesis indicates the  $T_g$  of the SAN-g

when the AN content in the matrix is higher than that of the graft. The span of AN differential that results in blends of superior properties becomes wider as the graft AN content is increased. At the same time the level of maximum tensile yield strength and toughness is also improved (see Table 6). The trends shown in Table 6 manifest the improved ductility in the matrix phase with increased AN level. Results from dynamic mechanical testing qualitatively correlate with the adhesive coupling between the components.

When using graft rubber particles of similar size and morphology, there are at least three major factors that influence the mechanical properties of SAN/SAN-g blends. They are: interfacial adhesion; state of rubber particle dispersion; and inherent ductility of matrix SAN. It is concluded that the inherent ductility of the matrix polymer provides a rational basis for understanding the properties of toughened SAN copolymers by SAN emulsion grafted rubbers. The first two depend on the

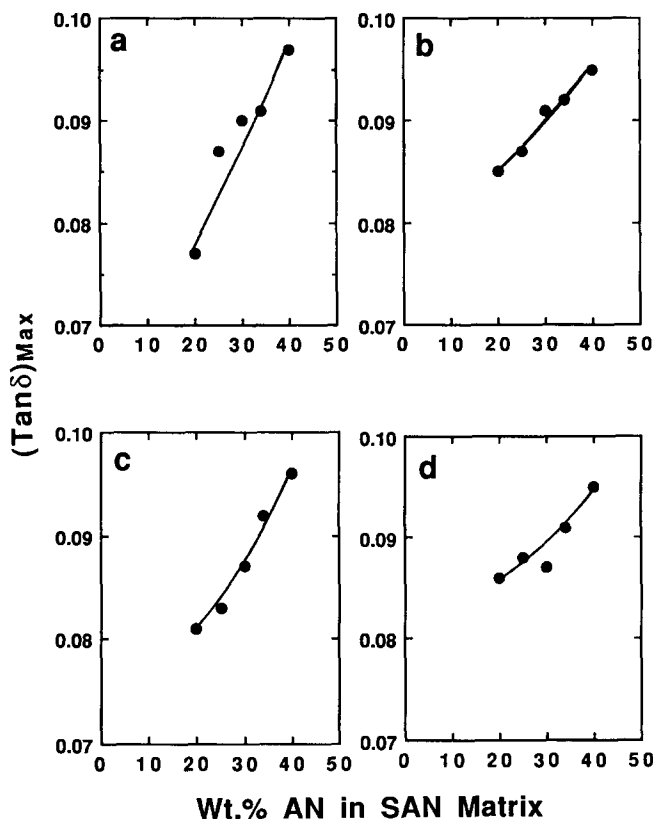


Figure 13 Maximum height of rubber damping peak  $(\tan \delta)_{\text{Max}}$  versus AN content of SAN matrix. All blends contain 30% rubber; (a) SAN-g-14.2; (b) SAN-g-16.9; (c) SAN-g-19.1; (d) SAN-g-22.0

Table 6 Summary of mechanical properties of SAN-g blends (all blends contain 30% rubber)

% AN in the graft of SAN-g	% AN in the matrix at optimum mechanical properties	$\Delta$ AN	Notched Izod impact strength (J/m)	Tensile yield strength (MPa)	Strain at break (%)
14.2	20	5.6	315	26.9	9.8
16.9	25	8.1	390	28.3	8.7
19.1	30	10.9	480	29.7	10.8
22.0	34	12.0	507	31.0	9.6



difference between the AN levels in the matrix SAN and the graft SAN while the latter depends on the absolute value of the AN content of the matrix. This simple picture accounts for the main trends in toughness shown by these blends.

#### ACKNOWLEDGEMENTS

The authors wish to thank Asahi Chemical Industry Co. Ltd for supplying the graft rubbers and several SAN copolymers. Thanks are also due to The Dow Chemical Company and Monsanto Company for the SAN copolymers. Transmission electron microscopy was carried out by T. W. Cheng. This research was supported in part by the US Army Research Office.

#### REFERENCES

- 1 Kim, H., Keskkula, H. and Paul, D. R. *Polymer* 1990, **31**, 869
- 2 Molau, G. E. *Polym. Lett.* 1965, **3**, 1007
- 3 Schwarz, M. C., Keskkula, H., Barlow, J. W. and Paul, D. R. *J. Appl. Polym. Sci.* 1988, **35**, 653
- 4 Dekkers, M. E. J. and Heikens, D. J. *Mat. Sci.* 1985, **20**, 3873
- 5 Keskkula, H., Kim, H. and Paul, D. R. *Polym. Eng. Sci.* 1990, **30**, 1373
- 6 Keskkula, H. unpublished results
- 7 Matsuo, M., Wang, T. T. and Kwei, T. K. *J. Polym. Sci. A-2* 1972, **10**, 1085
- 8 Kim, H., Keskkula, H. and Paul, D. R. submitted to *Polymer*
- 9 Bucknall, C. B. 'Toughened Plastics', Applied Science, London, 1977
- 10 Wu, S. J. *Appl. Polym. Sci.* 1988, **35**, 549
- 11 Kim, J. H., Keskkula, H. and Paul, D. R. *J. Appl. Polym. Sci.* 1990, **40**, 183
- 12 Ricco, T., Pavan, A. and Danusso, F. *Polymer* 1975, **16**, 685
- 13 Morbitzer, L., Kranz, D., Humme, G. and Ott, K. H. *J. Appl. Polym. Sci.* 1976, **20**, 2691
- 14 Aoki, Y. *J. Rheol.* 1981, **25**, 351
- 15 Aoki, Y. and Nakayama, K. *Polym. J.* 1982, **14**, 951
- 16 Aoki, Y. *Macromolecules* 1987, **20**, 2208
- 17 Masuda, T., Nakajima, A., Kitamura, M., Aoki, Y., Yamauchi, N. and Yoshioka, A. *Pure Appl. Chem.* 1984, **56**, 1457
- 18 McCrum, N. G. *J. Polym. Sci.* 1958, **27**, 555
- 19 McCrum, N. G. *J. Polym. Sci.* 1959, **34**, 355
- 20 McCrum, N. G. *Makromol. Chem.* 1959, **34**, 50
- 21 Matsuo, M., Wang, T. T. and Kwei, T. K. *J. Polym. Sci. A-2* 1972, **10**, 1085
- 22 Beck, R. H. Jr *J. Polym. Sci. B* 1968, **6**, 707
- 23 Wang, T. T., Matsuo, M. and Kwei, T. K. *J. Appl. Phys.* 1971, **42**, 4188
- 24 Schmitt, J. A. *IUPAC Symp.*, Toronto, 1968, Vol. 2, p. A9
- 25 Bohn, L. *Angew. Makromol. Chem.* 1971, **20**, 129
- 26 Turley, S. G. *J. Polym. Sci. C* 1973, **1**, 101
- 27 Murayama, T. and Lawton, E. L. *J. Appl. Polym. Sci.* 1973, **17**, 669
- 28 Chua, P. S. *Polymer Composites* 1987, **8**, 308