

Toughening of SAN copolymers by an SAN emulsion grafted rubber

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

Department of Chemical Engineering and the Center for Polymer Research, University of Texas at Austin, Austin, TX 78712, USA

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A series of styrene/acrylonitrile (SAN) copolymers have been blended with an SAN grafted butadiene rubber to form ABS type materials. The major focus has been the effects of composition of the SAN matrix copolymer, for a fixed SAN graft, on blend toughness, deformation behaviour and morphology. The AN content varied from 0 to 40% in the matrix copolymers, while the AN content of the emulsion-made graft was fixed at 22.5%. Maximum strength and toughness were observed for compositions based on SAN matrices containing 34% AN. Mechanical dilatometry revealed no major changes in deformation mechanism as the AN content of the matrix changed. Most of the deformation was due to dilatational processes, presumably crazing. Transmission electron photomicrographs, on the other hand, showed differences in rubber particle dispersion. The morphology revealed by scanning electron microscopy of fracture surfaces distinguished the ductile and less ductile blends. Issues relating to the miscibility of the component polymers and adhesion are discussed.

(Keywords: SAN copolymers; ABS type materials; physical properties; deformation behaviour)

INTRODUCTION

Rubber toughened styrene-acrylonitrile (SAN) copolymers are important commercial products. Sales of acrylonitrile-butadiene-styrene (ABS) polymers were nearly half a million tons in the US in 1986. The methods of ABS manufacture and studies of the variables affecting their mechanical properties have been the subject of a number of reviews and articles^{1,2}. The principal method of ABS manufacture involves the grafting of rubber seed latex with SAN. The matrix SAN may be produced during the grafting reaction or separately, followed by melt blending with the graft. Many hybrid processes are being used. A number of studies have been published that examine various seed and grafting variables, such as particle size, crosslinking and degree of grafting³⁻⁷. In these previous studies, the graft composition has usually been kept the same as that of the matrix SAN in order to achieve a high degree of compatibility between the SAN grafted to the rubber particles and the matrix.

The effects of varying the SAN matrix composition in blends with an SAN grafted emulsion rubber (designated as SAN-g) on the mechanical properties and morphology of the blends is the purpose of this paper. An important consideration here is the miscibility of the SAN graft with the matrix SAN. It is known that the miscibility of SAN copolymers depends on the difference in their acrylonitrile contents and their molecular weights^{8,9}. For blends of SAN copolymers having molecular weights typical of commercial products, the AN difference must be within about 5% before immiscibility is observed⁸. The interaction between the grafted rubber particles and the matrix is expected to be optimum when the styrene/acrylonitrile ratios in the two phases are nearly the same. Either a reduction or increase of the AN content in the matrix, relative to that in the graft, could, in principle,

lead to a reduced mechanical coupling between the two phases. Furthermore, phase separation between any free SAN from the graft and the SAN from the matrix is expected when the difference of the AN content exceeds about 5% at a molecular weight of 10^5 (ref. 8); see *Figure 1*. Because of these two effects, that is, reduced coupling of graft and matrix and phase separation of two SAN copolymers comprising the matrix, this paper explores the changes in morphology and in mechanical properties as the AN content of the matrix polymer is varied while

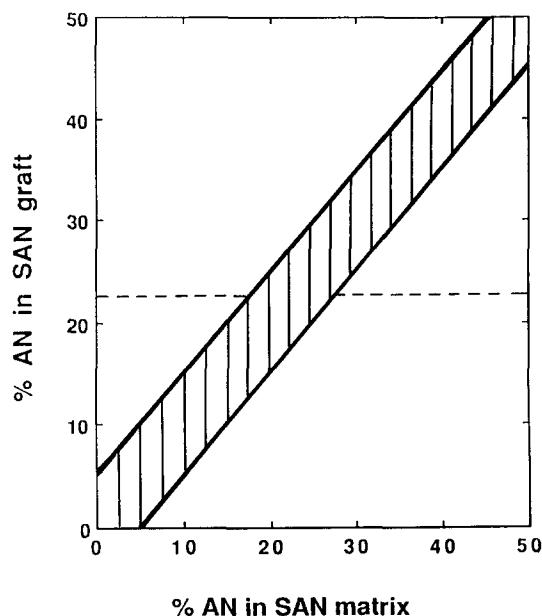


Figure 1 Phase behaviour of SAN copolymers applied to graft and matrix SAN materials. Shaded area shows miscible region for $M = 10^5$. The dotted line shows the composition of the single graft which has been blended with various SAN matrices in this work

* To whom correspondence should be addressed

Table 1 Matrix polymers used in this study

Percent AN			Molecular weight
0	PS	Styron 685D ^a	$\bar{M}_w = 300\,000$ $\bar{M}_n = 132\,000$
6.3	SAN6.3	Exp. polymer ^a	$\bar{M}_w = 343\,000$ $\bar{M}_n = 121\,000$
14.7	SAN14.7	Exp. polymer ^b	$\bar{M}_w = 182\,000$ $\bar{M}_n = 83\,000$
20	SAN20	XP 72006 ^a	$\bar{M}_w = 178\,000$ $\bar{M}_n = 88\,000$
25	SAN25	Tyrl 1000 ^a	$\bar{M}_w = 152\,000$ $\bar{M}_n = 77\,000$
30	SAN30	Tyrl 880 ^a	$\bar{M}_w = 168\,000$ $\bar{M}_n = 81\,000$
33	SAN33	Exp. polymer ^c	$\bar{M}_w = 146\,000$ $\bar{M}_n = 68\,000$
34	SAN34	Exp. polymer ^b	$\bar{M}_w = 145\,000$ $\bar{M}_n = 73\,000$
40	SAN40	Exp. polymer ^b	$\bar{M}_w = 122\,000$ $\bar{M}_n = 61\,000$

^a Provided by The Dow Chemical Co.^b Provided by Asahi Chemical Industry Co. Ltd^c Provided by Monsanto Co.**Table 2** SAN grafted rubber modifier used in this study (Sumitomo Naugatuck BL-65)

Gel phase, %	70
Butadiene, %	46
Rubber, %	50
G/R^a	0.4
Rigid phase, %	30
AN, %	22.5
M_n	44 000
M_w	167 000

^a $G/R = (\text{Gel}\% - \text{Rubber}\%)/\text{Rubber}\%$

the AN content of the graft is held fixed. It is of particular interest to study the changes in the impact strength of these blends, the mechanism of deformation by mechanical dilatometry, and the interfacial adhesion between SAN-g and matrix copolymers. Results from these experiments will be discussed and comparisons developed.

EXPERIMENTAL

Materials

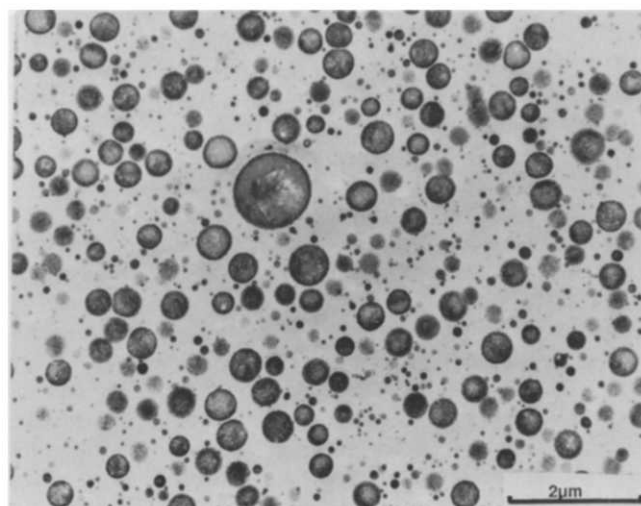
The various glassy matrix polymers used in this study, described in *Table 1*, were high molecular weight moulding grade materials. The characteristics of the SAN-g are summarized in *Table 2*, and its particle morphology is shown in *Figure 2*. The SAN-g material used as a modifier has been characterized in various ways, including extraction by methyl ethyl ketone with subsequent separation into a swollen gel phase (70% of the mass including rubber and chemically bound SAN) and an MEK soluble phase (30% of the mass consisting of 'free' SAN). As a whole, the material contains 50% rubber. This copolymer rubber has a 92% butadiene content. The remaining half is SAN of which 40% is bound to the rubber. The remaining 60% of the SAN, not bound to rubber, was determined to contain 22.5% AN and to have $M_n = 44\,000$ and $M_w = 167\,000$. The bound SAN is presumably similar to the free SAN; however, direct characterization of the former is exceedingly difficult.

Blend preparation

The 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 component polymers were dried overnight at 75°C before extrusion. Each blend of about 1500 g was extruded twice to ensure uniform mixing. The extruded pellets were dried again before compression moulding into 0.318 cm thick plaques.

MATERIAL TESTING

Tensile properties were determined on an Instron 1137 tester with a computerized data acquisition system at a crosshead speed of 0.508 cm/min. Notched Izod impact strength was measured according to ASTM D256-56 using a pendulum type tester. Five to ten bars were tested on each instrument. Standard deviations of 5% or less were found for stress, modulus and impact strength. For strain at break, standard deviation was found to be from 10 to 20% of the average value. Mechanical dilatometry was also carried out on a specially modified Instron machine, where a water-filled chamber is used to measure the volume change during extension. The details of this technique are given elsewhere¹⁰. Interfacial adhesion between SAN-g and various SAN copolymers was measured using a lap shear method. In every case, SAN was used for the two outer layers while the grafted butadiene rubber was the inner layer of the three-piece sandwich. The sheets of each polymer used to form this laminate were compression-moulded. Due to the brittleness of SAN outer layers, the SAN sheets were reinforced by impregnation of a Kevlar mesh fabric to prevent premature failure of the brittle polymer. The SAN outer layers were approximately 0.318 cm thick while the inner layer was approximately 0.038 cm thick. The three sheets were placed together in a mould and laminated at $130 \pm 3^\circ\text{C}$ under a pressure of 1.5 MPa for about 7 min to form the bond at the two interfaces. After lamination, 20.3 cm by 2.08 cm strips were cut and notched so that a lap shear joint of 1.03 cm² area was formed. The welding temperature and area of lap shear joint were chosen by trial and error. At high welding temperatures, most of the samples broke in the SAN outer layer rather than at the interface, so the welding

**Figure 2** Transmission electron photomicrograph of OsO₄ stained ultrathin section of rubber graft material (Sumitomo Naugatuck BL-65)

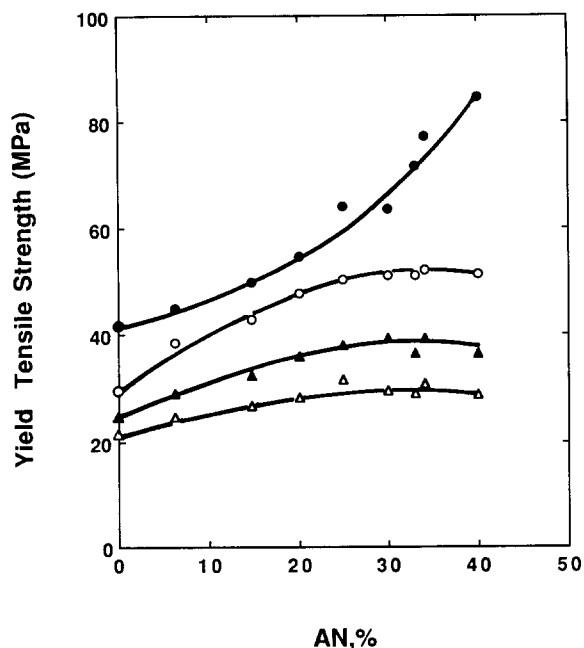


Figure 3 Yield tensile strength of blends at various rubber level versus percent AN in the matrix SAN: ●, 0% rubber; ○, 10% rubber; ▲, 20% rubber; △, 30% rubber

temperature was lowered and the joint area was reduced until failure did occur at the interface. Because of the effects of geometry and process conditions on the joint strength, the results shown are only meaningful for comparison among similar specimens. As will be shown, the small area of the lap shear joint is responsible for the relatively high values of the average adhesive strength in comparison to other systems¹¹. The basic principles of lap shear tests are given by Wu¹².

RESULTS AND DISCUSSION

The SAN-g described in Table 2 and Figure 2 is a commercial product manufactured by the Sumitomo Naugatuck Co. and used primarily for impact modification of poly(vinyl chloride). However, it has been found to be an excellent impact modifier for SAN as well¹³. Blends of this SAN-g, containing SAN with 22.5% AN, and commercially available SAN25 or SAN20 have sufficiently similar compositions and provide a basis for comparison with blends of SAN copolymers containing from 0% to 40% AN. The rubber levels in the blends were varied from 10 to 35%. At the 10% rubber level only minimal toughness was expected while blends containing 20–30% rubber represent typical ABS compositions available commercially.

Tensile and impact properties

The tensile properties of the blends are summarized in Figures 3–6. Figure 3 shows the tensile yield strength of the blends as a function of AN content of the matrix SAN at three different rubber concentrations. While there is a significant increase in yield strength of unmodified SAN copolymers with increasing AN content, rubber modified blends show relatively less sensitivity to AN content, particularly at higher rubber concentrations. The yield strengths of the blends gradually increase up to 25% AN and reach essentially a plateau value at each rubber level. Tensile yield strength of composite materials

is a combined property determined by the strength of each component and the bond between the components¹⁴. In some cases it can be considered as a qualitative indication of stress transfer level between the components of a composite material. In the present case, it is interesting to compare Figure 3 with the results of the adhesion tests shown in Figure 10. A similar trend is observed. In addition to this comparison, the stress

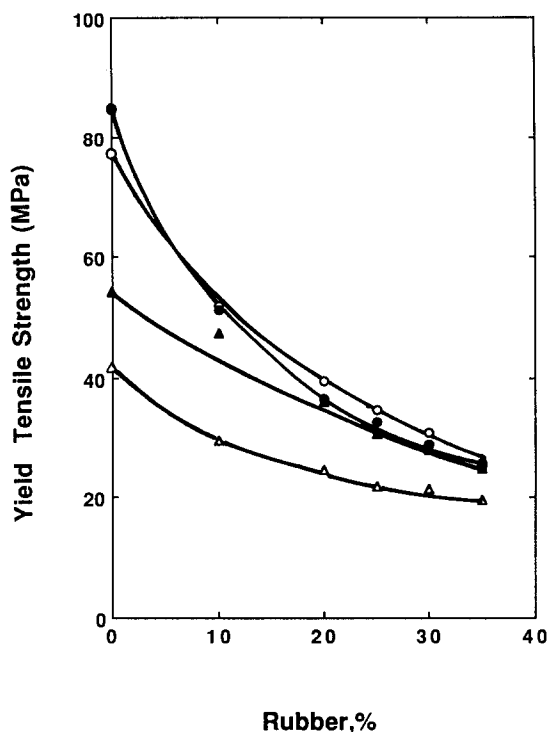


Figure 4 Yield tensile strength versus % rubber for blend based on various SAN matrices: △, PS; ▲, SAN20; ○, SAN34; ●, SAN40

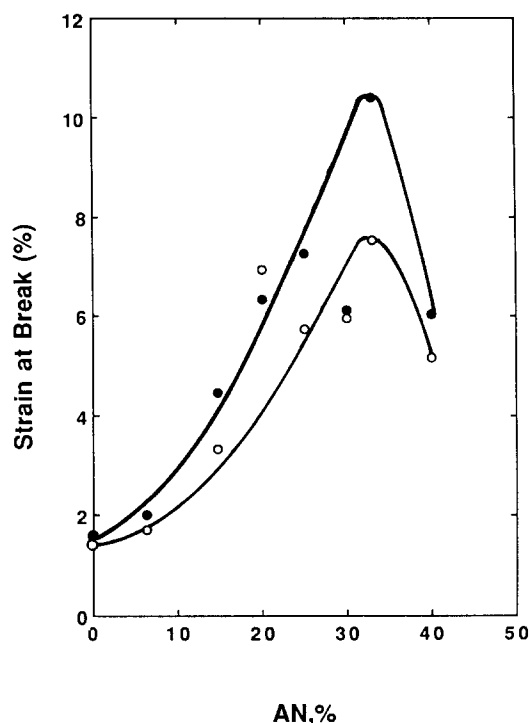


Figure 5 Strain at break versus percent AN of matrix SAN for two levels of rubber: ○, 20% rubber; ●, 30% rubber

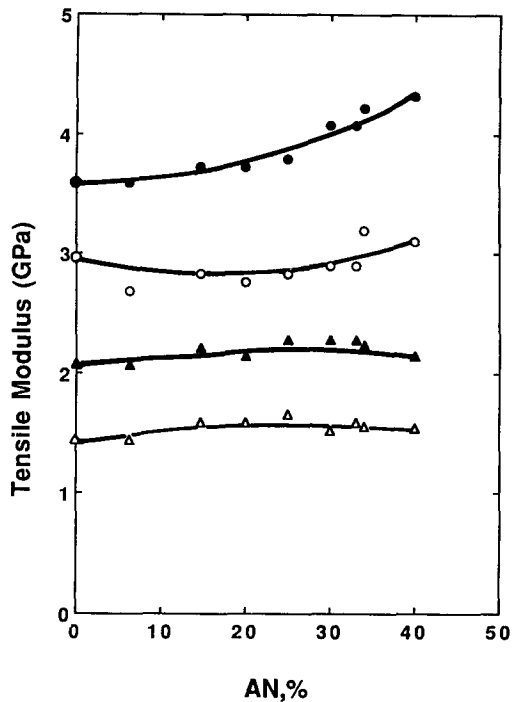


Figure 6 Tensile modulus versus AN content of matrix SAN at various rubber levels: ●, 0% rubber; ○, 10% rubber; ▲, 20% rubber; △, 30% rubber

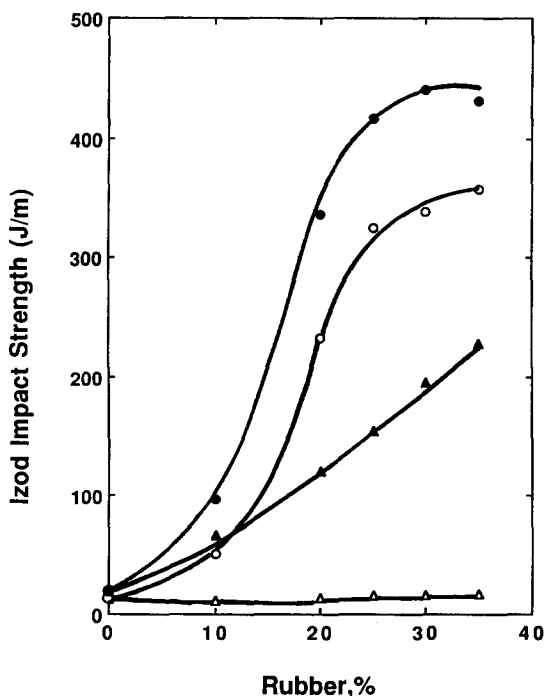


Figure 7 Notched Izod impact strength versus percent rubber content for various SAN matrices: △, PS; ○, SAN20; ●, SAN34; ▲, SAN40

concentration effect of the rubber phase and the degree of its dispersion (see Figure 11) will undoubtedly affect the yield strength of the blend. In Figure 4, the yield tensile strength is shown as a function of the rubber content of the blends. A sharp drop occurs initially, but beyond 20% rubber loading the rate of change is relatively small. The blends with SAN34 typically show the highest values. The strain at break is shown in Figure 5 as a function of AN content for two different rubber levels. This quantity is more sensitive than other tensile

properties. It is interesting to note that the strain at break shows a maximum value at about 34% AN content. In tensile tests, the fracture of the blends occurs after a significant stress-whitening and at a lower level of stress than at yield, indicating considerable ductility and stress softening, typical of high impact polymers. Figure 6 shows the strong influence of the rubber phase on the tensile modulus. The addition of the first 10% of rubber causes the largest drop in modulus. There is very little change in modulus as the AN content is changed for any given rubber level.

While notched Izod impact strength gives only limited information about complex high speed failure of materials, it is one of the most widely used measures of polymer toughness. Accordingly, notched Izod impact strengths were determined at room temperature for all compositions and are shown in Figure 7 as a function of rubber content. While the PS based blends show essentially no increase in toughness regardless of the rubber concentration, the other blends show a significant increase in impact strength above 10% rubber. Again SAN34 blends show the greatest toughness at all rubber concentrations. All of the blends except those based on PS and SAN6.3 showed some improvement in toughness on addition of the impact modifier. Figure 8 shows the effect of the matrix composition on toughness at 20 and 30% rubber levels. It is clear that at both rubber levels the impact strength is maximum at about 34% of AN in the matrix copolymer. The close agreement for SAN33 and SAN34, obtained from different sources, adds confidence that the maximum toughness is at about 34% AN.

It is important to note that blend mechanical properties steadily improve with increasing AN content of the matrix up to 34% AN. The highest levels of tensile

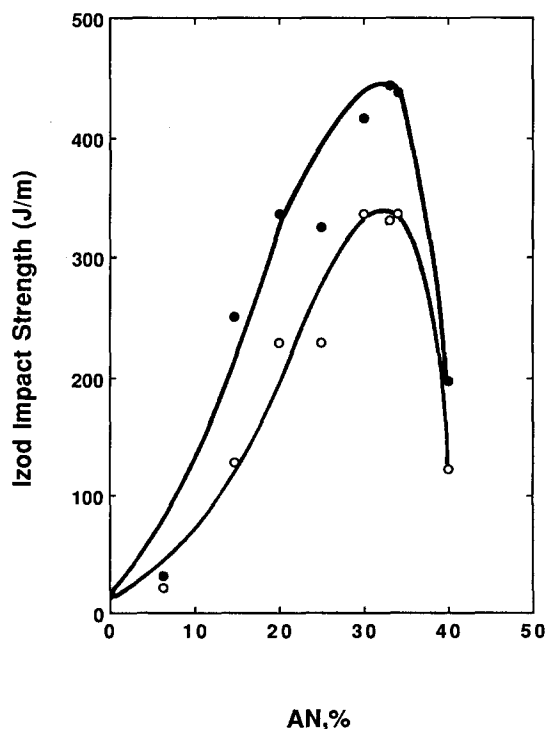


Figure 8 Notched Izod impact strength versus percent AN of the SAN matrices for two levels of rubber content: ○, 20% rubber; ●, 30% rubber

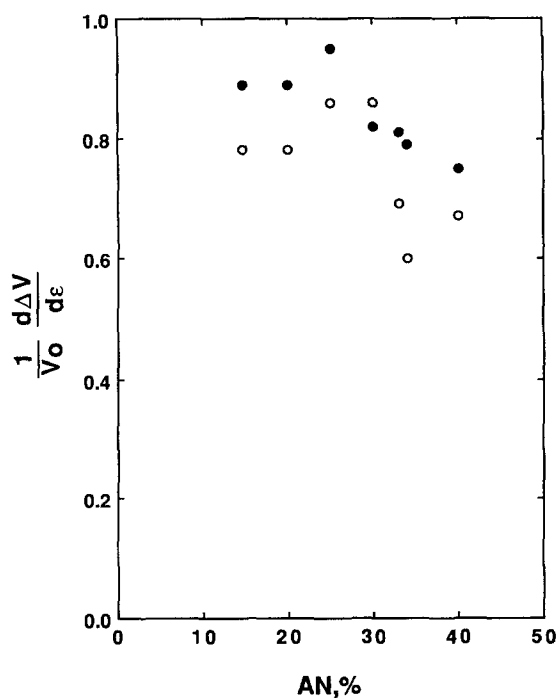


Figure 9 Slope of post-yield volume strain *versus* axial strain for blends containing two levels of rubber as a function of percent AN of SAN matrix: ●, 20% rubber; ○, 30% rubber

strength, strain at break and impact strength are all achieved simultaneously with blends containing SAN34. On the other hand, the matrix polymers which most closely match the AN level in the graft, namely SAN20 and SAN25, develop only intermediate property levels. Apparently some mismatch in the AN levels of the graft and of the matrix is not necessarily harmful. Note, however, that SAN34 and SAN14.7 are not expected to be miscible with the SAN of the graft containing 22.5% AN because these correspond to an AN difference of 11.5% and 7.8% respectively.

This may lead to several consequences. First, one intuitively expects better adhesion between two SAN copolymers if they are miscible and that some degree of adhesive coupling of the matrix and graft material is required to develop toughness. In a later section, we will quantify the effect of AN difference on adhesion. Second, the free SAN of the graft material and the SAN matrix could form a separate phase if the former were to leave the region of the graft SAN chains. Generally, such phase separation is expected to be detrimental to mechanical properties depending on adhesion at the interface between the two phases. Another factor that enters the picture here is the inherent ductility or the propensity of the matrix material to be toughened. We believe that within the range considered here the inherent ductility of these SAN copolymers increases with AN content. Direct information on this issue would be most helpful and attempts to address this question are in progress.

Deformation behaviour

Measurement of the post yield volume changes by using a liquid displacement stress dilatometer is an effective tool for determining the deformation mode of polymer systems^{10,15,16}. This technique is able to determine the relative contribution of shear deformation *versus* dilatational (crazing, delamination, hole formation, etc.) modes of deformation during uniaxial elongation.

This information is given by the slope of the volume strain *versus* axial strain experienced by the sample after yield. The extreme cases are purely dilatational (slope = 1) and nondilatational (slope = 0) processes. Crazing, as in HIPS, is a dilatational process while shear yielding is a nondilatational or constant volume process. For mixed modes of shear deformation and dilatational processes, slopes between 0 and 1 are to be expected.

Figure 9 summarizes data from mechanical dilatometry showing that the deformation process during tensile testing is almost entirely dilatational and probably caused by crazing with possibly some hole formation within the rubber particles. However, a small portion of shear yielding does contribute to the deformation process especially as the AN content of the SAN matrix increases over 30%. As suggested by the observations by Dekkers and Heikens¹⁷, it appears that this small amount of shear band formation occurs at the expense of craze formation at high AN levels. There is no major transition in deformation mode even though impact strength varies strongly with matrix AN level. For example, at 30% rubber the impact strength of the SAN30 blend is almost twice that of the SAN14.7 blend yet both blends deform predominantly by a dilatational process. This significant change in toughness does not correspond to a major change in deformation mechanism as measured at the speed of 0.508 cm/min.

Interfacial adhesion

As mentioned earlier, it is believed that some critical level of adhesion between the SAN matrix and the rubber phase is needed to achieve toughness. This adhesion level is assured when the grafted SAN chains are miscible with the matrix SAN. However, if the AN difference between the two is greater than the limit for miscibility (see Figure 1), then the question of adhesion must be addressed. This was done here by bonding the various SAN matrix materials to compression moulded sheets of the modifier whose surface should be predominantly SAN. Figure 10 shows the lap shear strength for SAN/SAN-g joints as a

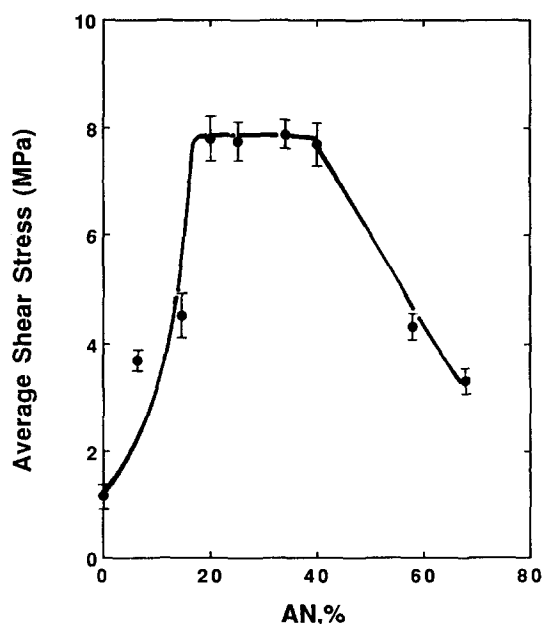


Figure 10 Average lap shear adhesive strength of joints formed from SAN-g and SAN matrix copolymers as a function of AN content of latter

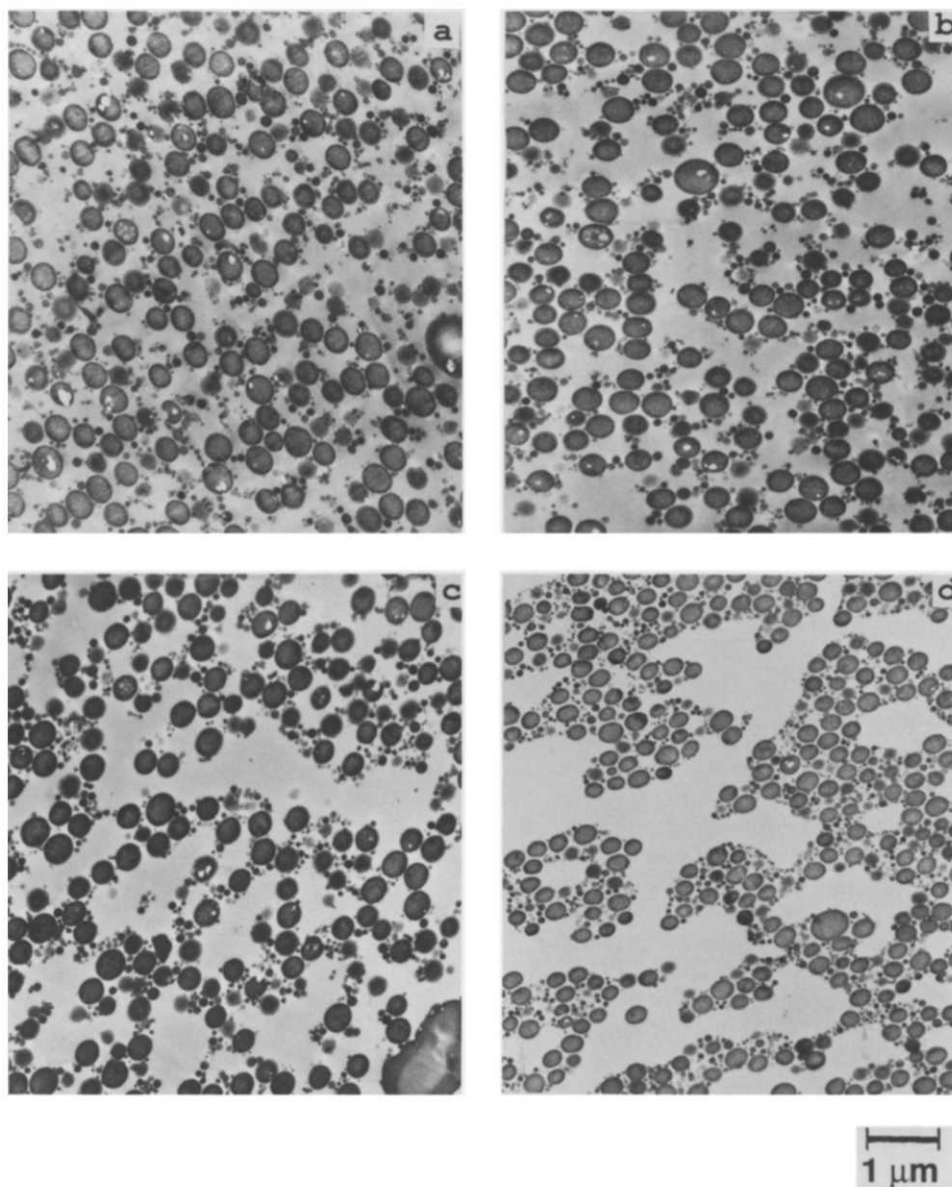


Figure 11 Transmission electron photomicrographs for blends: (a) SAN20 (2.5%); (b) SAN34 (11.5%); (c) SAN40 (17.5%); (d) PS (22.5%). All blends contain 30% rubber. Numbers in parentheses indicate the difference in percent AN of the SAN-g and the matrix SAN

function of percent AN in the SAN. SAN copolymers containing up to 68% AN were used in this experiment in order to define clearly the span of AN contents where an adequate level of adhesion prevails. The average shear stress required for failure at the interface is significantly increased as the AN content is increased and it reaches a plateau value for SAN copolymers containing between 20% and 40% AN. Good adhesion levels are expected for AN levels in the matrix that lie within the miscibility range (see *Figure 1*) centred about the AN content of the SAN graft. However, the data in *Figure 10* indicate that comparable levels of adhesion persist outside this range, no doubt owing to significant interpenetration of segments across the phase boundary between the two immiscible SAN copolymers.

Phase and fracture morphology

Transmission electron photomicrographs for selected blends having major differences in ductility are shown in *Figure 11*. The size and shape of the rubber particles in

the blends are quite similar to the SAN-g itself which indicates that no dramatic change in the structure of the rubber particles occurred during blending. However, some significant changes in the state of dispersion of the rubber particles are seen as the AN level of the matrix varies. As the difference in AN content of the graft and the matrix copolymers increases, the rubber particles appear to be more agglomerated with large areas of the matrix free of particles. While the blend with SAN20 shows a relatively good state of dispersion, the blend with PS shows strongly agglomerated rubber particles. These differences in rubber particle dispersion can be easily understood in terms of the miscibility of the graft and the matrix copolymers. It must be recalled that 60% of the SAN associated with the impact modifier (22.5% AN) is not chemically bound to the rubber particles. If this free SAN is not miscible with the matrix SAN (see *Figure 1*) and the two form separate phases, then the rubber particles are more likely to reside in the free SAN phase because the attached SAN chains are presumed to

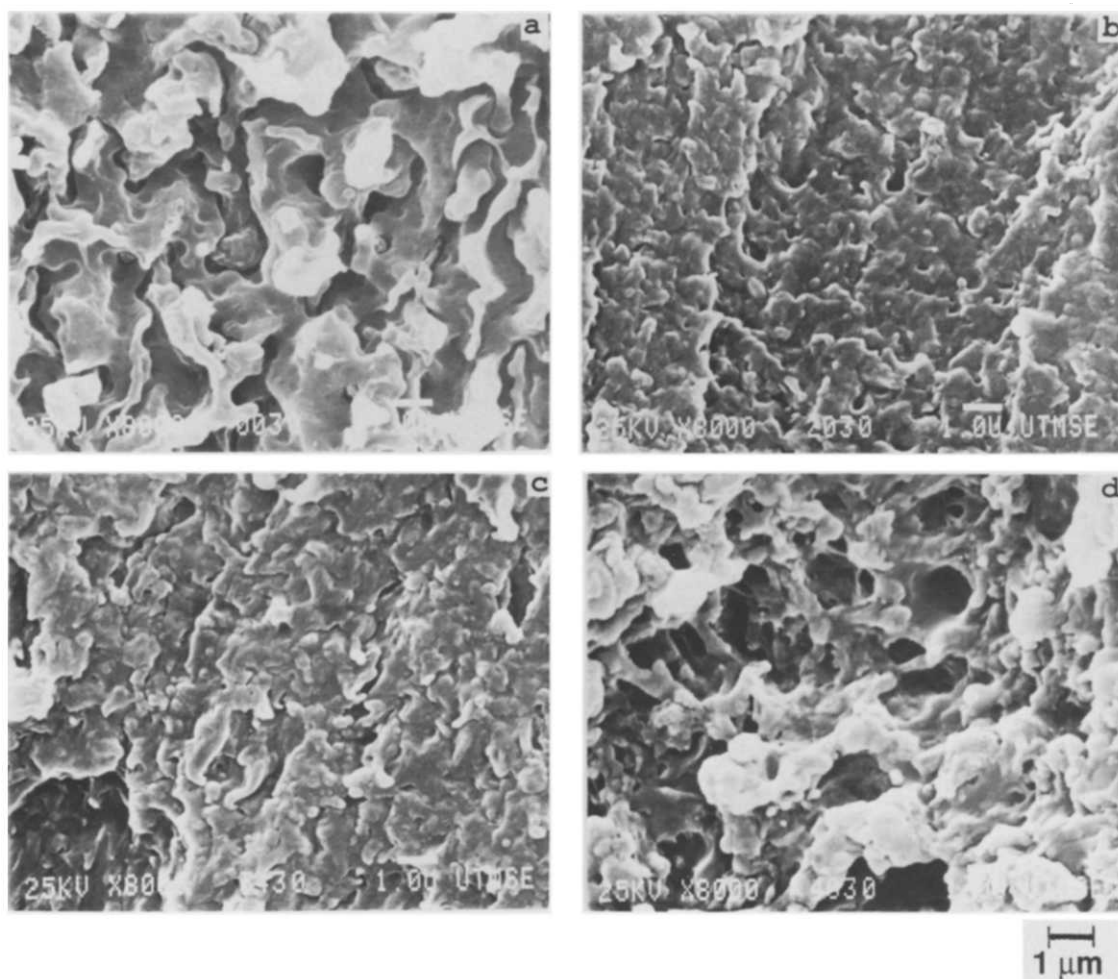


Figure 12 Scanning electron photomicrographs of fracture surfaces of blends: (a) PS (16.0 J/m); (b) SAN20 (328.8 J/m); (c) SAN34 (439.9 J/m); (d) SAN40 (195.4 J/m). All blends contain 30% rubber. Specimens were fractured in an Izod tester at room temperature, and numbers in parentheses show notched Izod impact strength

be identical in AN level. Therefore, one interpretation of the lower two photomicrographs shown in *Figure 11* is that the zones devoid of the rubber particles are separate phases formed by the matrix material, SAN40 in *Figure 11c* and PS in *Figure 11d*, which the graft shells of the particles find thermodynamically inhospitable relative to a phase consisting of free and grafted SAN containing 22.5% AN. The situation would be different if the modifier consisted of true shell/core particles having no free SAN. However, even here particle-particle contacts are favoured and can lead to a tendency for agglomeration, but effective mixing protocols may, in principle, lead to more uniform dispersion.

Recently, Wu has proposed that the thickness of matrix ligaments is the single parameter determining whether a rubber-modified nylon blend will be tough or brittle¹⁸. According to his model, it was predicted that particle agglomeration greatly reduces the toughening efficiency of rubber and that fine dispersion of particles is a prerequisite for toughening. In the present case, blends with SAN34, which have the highest impact strength, show some agglomeration of rubber particles. Although the degree of agglomeration in SAN34 blend is not as great as that in PS, the state of dispersion is not as good as that seen in the SAN20 blend. Extreme agglomeration, like that for PS or SAN40 blends, is apparently detrimental to toughness; however, the rubber/polymer

blends considered here are complicated by the separate matrix phase mentioned earlier. Nevertheless, it must be emphasized that the uniform dispersion of rubber particles is not always a requirement for maximizing toughness, because examples of agglomerated structures showing better impact strength than well dispersed mixtures will be discussed¹⁹.

Figure 12 shows fracture surfaces of the blends obtained using scanning electron microscopy. The ductile blends shown in *Figure 12b* and *c* and the less ductile blends shown in *Figure 12a* and *d* clearly differ in certain topological features of their fracture surface. The materials showing less ductile behaviour have more irregular surfaces and frequent large holes. Comparing these fracture surfaces with corresponding TEM photomicrographs in *Figure 11*, one observes that the more brittle compositions show considerable agglomeration of rubber particles and there is an indication of less interaction between the graft and matrix polymer. The toughest blends show a rather homogeneous surface with no large holes. The surface of the tough blends show indications of plastic flow during the fracture process not observed with more brittle blends.

SUMMARY AND CONCLUSIONS

The most interesting result of this work is that optimum

toughness for blends with a single SAN (22.5%) grafted emulsion rubber occurs when the added SAN contains about 33–34% AN. Such blends would be useful as ABS materials with a superior solvent and stress–crack resistance.

Based on simple considerations, maximum mechanical coupling of the matrix and rubber particles is expected when the AN levels of the SAN chains are exactly matched or, at least, are within the miscibility region. However, lap shear measurements indicate that adequate adhesion is obtained over an even broader range of AN differences. A plausible hypothesis is proposed to explain this mismatch in AN levels for maximum toughness. Based on available information and experience, the ability of an SAN copolymer to be toughened, or its intrinsic ductility, seems to increase continuously with increased AN level over the range considered here.

Because adequate adhesion is obtained for a finite AN differential, broader than the miscibility range, maximum toughness occurs at the highest matrix AN levels not limited by adhesion to the graft or some other cause. The decline in toughness at higher levels of matrix AN may result from a failure to achieve a uniform distribution of rubber throughout the systems because of phase separation between the added SAN and the free SAN associated with the grafted matrix rather than a loss in adhesion to the grafted rubber particles.

Future work needs to focus on several directions to clarify these issues. First, there needs to be a more quantitative assessment of the proposed increased propensity for toughening of SAN as AN level increases. Second, it would be useful to vary the AN content of the graft SAN rather than that of the matrix. Third, it would be especially interesting to examine the dispersibility of grafted rubber particles having no free SAN in various matrices with the hope that the issue of rubber–matrix adhesion can be dealt with independently of issues of phase segregation and agglomeration.

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