# Morphology and Physical Properties of SAN/NBR Blends: The Effect of AN Content and Melt Viscosity of SAN

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ABSTRACT: To study the effect of dispersed poly(butadiene-*co*-acrylonitrile) (NBR) rubber size on the physical properties of poly(styrene-*co*-acrylonitrile) (SAN)/NBR blends, SANs with various melt viscosities and acrylonitrile (AN) contents were examined. The dispersed size of NBR, whose AN content is 30 wt %, was reduced as the melt viscosity of the SAN matrix was increased or as the AN content of the SAN matrix was reduced in the range of 19–32 wt %. As the melt viscosity of the SAN matrix was increased, the damping peak of the NBR phase moved to a higher temperature, and as the AN content of SAN was reduced, the damping peak of the SAN phase moved to a lower temperature. Higher values of impact strength and elongation at break and reduced yield behavior at a low shear rate were observed at a finer dispersion of NBR. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 935–941, 1999

Key words: SAN; NBR; blend; rubber size; melt viscosity; AN content; impact strength

# INTRODUCTION

It is well known that the size and the shape of the dispersed rubber phase in a rubber–plastic blend are important factors that determine the mechanical properties of rubber-toughened plastics.<sup>1</sup> During the melt processing, the minor rubber phase is broken up, and the morphological structure of the dispersed rubber phase is generated *in situ*. Interfacial and rheological factors, such as interfacial tension, shear rate, viscosity ratio of the dispersed rubber phase, and the matrix, are important factors that should be considered for controling the morphology of the dispersed rubber phase.<sup>2–4</sup> Poly(butadiene-*co*-acrylonitrile) (NBR)

is an important modifier of poly(styrene-co-acrylonitrile) (SAN), or acrylonitrile–butadine–styrene copolymer (ABS), to improve the impact strength or mat surface appearance.<sup>5,6</sup> Despite the commercial usefulness of these NBR/SAN or NBR/ABS blends, published articles that can give systematic information about interfacial or rheological factors to design optimum physical properties of these blends are not many.<sup>7,8</sup> In the present article, we report some results about the effect of the acrylonitrile (AN) content and melt viscosity of SAN on the physical properties of the SAN/NBR blends.

## EXPERIMENTAL

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Commercial grades of SANs, with the physicochemical properties listed in Table I, were used as

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	SAN1	SAN2	SAN3	SAN4	SAN5
Acrylonitrile content (wt %)	32	32	32	25	19
Melt flow index <sup>a</sup> (g/10 min)	67.4	27.5	16.2	28.1	5.5
Izod impact strength $(kg \cdot cm/cm)$	1.1	1.2	1.3	1.5	2.0
Tensile yield strength (kg/cm <sup>2</sup> )	760	800	830	700.6	
Elongation at break (%)	2.4	2.5	2.8	4.2	
Flexural strength (kg/cm <sup>2</sup> )	1220	1350	1460	1206	
Flexural modulus (kg/cm <sup>2</sup> )	37115	38040	39004	34605	
Vicat softening temperature (°C)	100.3	100.7	100.9	100.6	

Table I Composition and Physical Properties of SAN

<sup>a</sup> Measured at 220°C with 10 kg load.

received. The NBR, supplied by Bayer, was a commercial product named P30.49. Its AN content is 30 wt % and Mooney viscosity (ML<sub>1+4</sub> at 100°C) is 49. The complex viscosities of these polymers are shown in Figure 1.

Dried resins were hand mixed thoroughly at proper compositions and melt blended with a corotating twin-screw extruder (Berstorff ZE25, L/D = 33) at a zone temperature profile of  $190-210^{\circ}$ C and 250 rpm. Extrudates were quenched in water and pelletized. After drying at 80°C for 3 h, it was injection molded with a Dongshin Promax 150 injection molding machine. The machine was set at a barrel temperature profile of  $210-220^{\circ}$ C and a mold temperature of  $50^{\circ}$ C.



**Figure 1** Complex viscosity versus frequency of  $(\bullet)$  SAN1,  $(\bigcirc)$  SAN2,  $(\blacktriangledown)$  SAN3,  $(\bigtriangledown)$  SAN4,  $(\blacksquare)$  SAN5, and  $(\Box)$  NBR.

Morphology of the injection-molded specimen was observed with a scanning electron microscope (SEM, JEOL JSM820). SEM micrographs were taken from the cryogenically fractured surfaces, which were sputtered with gold before viewing.

Viscoelastic properties were measured with an Advanced Rheomtrics Expansion System (ARES, Rheomtrics). A temperature sweep from -100 up to 150°C was carried out, with a heating rate of 3°C/min, using solid-state torsion rectangular geometry for the specimen of  $12 \times 30 \times 1.6$ -mm<sup>3</sup> dimensions. The forced constant amplitude torsion strain was 0.3%, and the fixed oscillation frequency was 6.28 rad/s.

Melt rheological properties were measured with a parallel plate fixture. The frequency sweep was done with 15% strain, which is the upper limit where the linear viscoelastic behavior was maintained.

One-eighth inch notched Izod impact strength, Charpy impact strength, Vicat softening temperature (VST) at the load of 5 kg, tensile strength, and flexural strength were determined according to the ASTM D256, DIN 53456, ASTM D1525, D638, and D790, respectively.

## **RESULTS AND DISCUSSION**

Wu<sup>1</sup> showed that in many polymer/rubber blends where the rubber has a higher viscosity than the polymer, the number-average particle diameter,  $a_n$ , of the dispersed rubber phase can be described by the following equation:

$$a_n \propto \frac{4\gamma}{G \cdot \eta_m} \left(\frac{\eta_d}{\eta_m}\right)^{0.84}$$
 (1)

where G is the shear rate,  $\gamma$  the interfacial tension,  $\eta_m$  the matrix viscosity,  $\eta_d$  the disperseddrop viscosity.



**Figure 2** Scanning electron microphotographs of SAN/NBR (70/30 by weight) blends: (a) SAN1/NBR, (b) SAN2/NBR, (c) SAN3/NBR.

## The Effect of SAN's Melt Viscosity

Equation (1) suggests that  $a_n$  will be reduced as  $\eta_m$  is increased up to a value of  $\eta_d$  and the viscosity ratio,  $\eta_d/\eta_m$  approaches unity. In our SAN/NBR blend system, NBR has a much higher melt viscosity than SANs (Fig. 1). So, the size of the dispersed NBR droplet will be reduced as the melt viscosity SAN matrix is increased. This can be seen in Figure 2. Figure 2 shows that the size of

the void in the rubber phase, created during the fracturing process by the crazing of the rubber phase for energy absorption,<sup>9</sup> reduces as the melt viscosity of the SAN matrix is increased. This shows that the size of the dispersed NBR droplet is reduced as the melt viscosity of the SAN matrix is increased. In Figure 2, we can also see that the deformation of the dispersed rubber phase by the shear force during injection is most evident in Figure 2(c). This seems to be due to the fact that droplet deformation is enhanced with a higher viscosity of the matrix.<sup>10</sup>

The variations of dynamic mechanical properties, according to the change of the SAN matrix viscosity, are shown in Figure 3. In Figure 3, the damping peak of the SAN phase at 106°C does not show any variation; however, the damping peak of the NBR phase near -34°C moves to a higher temperature as the melt viscosity of the SAN matrix is increased. This suggests that the partial dissolution of SAN into the NBR phase is enhanced, and the thickness of the SAN/NBR mixed phase at the interface with a gradual concentration gradient is increased as the melt viscosity of the SAN matrix is



**Figure 3** Dynamic mechanical properties of SAN/NBR (70/30 by weight) blends: (—) SAN1/NBR, ( $\cdots$ ) SAN2/NBR, (--) SAN3/NBR.



**Figure 4** Storage shear modulus versus frequency of SAN/NBR (70/30 by weight) blend at (a) 180°C and (b) 240°C: ( $\bullet$ ) SAN1/NBR, ( $\bigcirc$ ) SAN2/NBR, ( $\checkmark$ ) SAN3/NBR.

increased.<sup>11,12</sup> In the rubber droplet-dispersed polymer systems, storage shear modulus (G') or loss shear modulus (G'') curves exhibit the second plateau at the low-frequency region.<sup>13</sup> It has been re-

ported that this yielding at the low-frequency region is due to the three-dimensional network created by the interacting droplets of the dispersed phase,<sup>14,15</sup> and this phenomenon is more evident in G' than in G''.<sup>16</sup> In G' versus the  $\omega$  plot of the SAN/NBR blends shown in Figure 4, we can observe that the yield behavior at low frequency is more evident when the matrix SAN's viscosity is inherently low [the SAN1/ NBR blend compared with the SAN3/NBR blend in Fig. 4(b)], or is lowered by raising the measuring temperature [Fig. 4(b) compared with Fig. 4(a)]. This shows that the three-dimensional network structure of the dispersed NBR droplet can be formed more easily when the melt viscosity of the SAN matrix is lowered.<sup>13</sup> For rubber-toughened plastics, a broad range of mechanical property behavior is expected, depending on the morphology of the dispersed rubber phase. The mechanical properties of our SAN/NBR(70/30 weight) blends are show in Table II, where we can see that both the Izod and Charpy impact strengths increase according to the kind of SAN by the order SAN1 < SAN2< SAN3. Because the large rubber particles are more effective in initiating the crazing, and small ones are more effective in initiating the yielding, the optimum rubber particle size depends on the intrinsic craze/yield behavior of the matrix.<sup>17,18</sup> The optimum rubber diameter for toughening SAN was reported to be 0.3 or 0.75  $\mu$ m.<sup>9,17</sup> In Figure 2, we can see that the size of the dispersed rubber particle is larger than 1  $\mu$ m in all three photographs, and the size decreases as the melt viscosity of the SAN matrix is increased. This reduction of the rubber particle down to the optimum size by the increased melt viscosity of the SAN matrix seems to be the cause of the enhanced impact strength. In Table II, we can also see that all other mechanical properties also increase as the dispersed rubber size is decreased by the increased melt viscosity of the SAN matrix, according to the order SAN1 < SAN2

Table II	Mechanical	<b>Properties</b>	of SAN/NBR	Blends
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	SAN1/NBR	SAN2/NBR	SAN3/NBR	(SAN2/SAN4)/NBR	SAN4/NBR
Izod impact strength $(kg \cdot cm/cm)$	6.0	8.5	12.0	12.2	14.0
Charpy impact strength (kJ/m <sup>2</sup> )	3.4	4.8	8.9	9.4	13.8
Tensile yield strength (kg/cm <sup>2</sup> )	373.2	417.2	436.9	412.5	404.2
Elongation at break (%)	5.5	7.6	13.6	10.7	12.0
Flexural strength (kg/cm <sup>2</sup> )	489.4	549.5	567.9	527.9	514.0
Flexural modulus (kg/cm <sup>2</sup> )	16658.5	17351.3	17231.5	17100.0	16943.4
Vicat softening temperature (°C)	77.2	77.3	80.5	75.0	72.6

 $^{\rm a}$  Measured at 220°C with 10 kg load.



**Figure 5** Scanning electron microphotographs of SAN/NBR blends: (a) SAN4/NBR (70/30), (b) (SAN2/SAN4)/NBR [(35/35)/30], (c) SAN2/NBR (70/30 by weight).

< SAN3, as in the behavior of the impact strength. Inherent physical properties of the SAN matrix and rubber size seem to give a complicated influence on these properties.

## The Effect of SAN's AN Content

In random copolymer blends, the miscibility behavior changes systematically as the relative composition of the constituent repeating units in the ran-

dom copolymer varies.<sup>19,20</sup> Many studies have been devoted to the miscibility behavior of SAN with other polymers because SANs with various AN contents are easily available as commercial polymers.<sup>21,22</sup> About the SAN/NBR blend, Cowie et al.<sup>8</sup> reported the detailed miscibility behavior in the broad range of copolymer compositions, and from the miscibility map of this article we could read that NBR with a 30 wt % AN content will not be miscible with any kind of SANs; however the partial miscibility will be enhanced as the AN content in the SAN is reduced down to about 15 wt %. So, in the SAN2/NBR (70/30 by weight), (SAN2/SAN4)/NBR [(35/35)/30 by weight], and SAN4/NBR (70/30 by weight) blends, we examined the effect of an average AN content in the SAN on the morphology and properties of SAN/NBR blends at a similar melt index of the SAN matrix.

Figure 5 shows the SEM microphotographs of these blends, where we can see that the dispersed rubber particle size reduces as the average AN content in the SAN is decreased. This reduction of  $a_n$  in eq. (1) shows that the  $\gamma$  is reduced due to enhanced



**Figure 6** Dynamic mechanical properties of SAN/ NBR (70/30 by weight) blends: (—) SAN2/NBR, (·····) SAN4/NBR.



**Figure 7** Storage shear modulus versus frequency of SAN/NBR blend at (a) 180°C and (b) 240°C:  $(\bigtriangledown)$  SAN4/NBR (70/30), ( $\checkmark$ ) (SAN2/SAN4)/NBR [(35/35)/30], ( $\bigcirc$ ) SAN2/NBR (70/30 by weight).

partial miscibility at a lower average AN content, because other rheological factors were similar.

In Figure 6, we can see that the damping peak of the SAN4 phase at 105°C appears at a slightly lower temperature than that of the SAN2 phase, whereas the damping peak of the NBR phase appears at the same temperature in both the SAN2 and SAN4 blends with NBR. This suggests the enhanced partial dissolution of NBR into the SAN phase when the AN content of SAN is reduced from 32 to 25 wt %.

In Figure 7, we can see the yield behavior at a high measuring temperature, and this yield behavior is more evident when the average AN content in the SAN is increased from 25 to 32 wt %. This suggests that the three-dimensional network structure of the dispersed NBR droplet can be formed more easily when the droplet size is larger at a higher AN content.

The variation of mechanical properties of SAN/ NBR (70/30 by weight) blends by the different AN content in SANs at a similar melt index of SAN can be observed in Table II with the SAN2/NBR (70/30 by weight), (SAN2/SAN4)/NBR [(35/35)/30 by weight], and SAN4/NBR (70/30 by weight) blends. The impact strength and elongation at break increase according to the order, SAN2 < (SAN2/SAN4  $\leq SAN4$  blends, as the dispersed NBR rubber size is reduced (Fig. 4) at a lower AN content in the SAN. This variation of impact strength and elongation at break is similar as in the previous discussion of the SAN1, SAN2, and SAN3 blends with NBR, where these properties were also enhanced when the NBR rubber size was reduced by the higher melt viscosity of the SAN matrix. However, other mechanical properties in Table II generally decrease according to the order, SAN2 > (SAN2/SAN4) > SAN4 blends, as the dispersed NBR particle size is reduced at a lower AN content in the SAN, contrary to the previous discussion of SAN1, SAN2, and SAN3 blends where those properties were enhanced at a smaller NBR particle size. These opposite trends in the variation of those mechanical properties seem to be due to the fact that these properties are complicatedly influenced by the inherent properties of the SAN matrix and the size of the dispersed NBR.

#### The Effect of Rubber Content

In Figure 8, a very fine dispersion of NBR in the SAN5 matrix can be observed. The melt viscosity of SAN5 is higher, and its AN content is lower



**Figure 8** Scanning electron microphotographs of SAN5/NBR (70/30 by weight) blends.



**Figure 9** The variation of (a) Izod impact strength, and (b) elongation at break according to the content of NBR in the blends of NBR with ( $\bigcirc$ ) SAN1, ( $\bigtriangledown$ ) SAN3 and ( $\blacksquare$ ) SAN5.

than any other SANs used in our study. These seem to be the cause of the fine dispersion of NBR.

In the previous discussion of the SAN/NBR (70/30 by weight) blends, impact strength and elongation at break were improved by the smaller size of the NBR, which was controlled by a rheological factor or an interfacial tension. To show the effect of the NBR size at a broad range of rubber content, the variation of these two physical properties, Izod impact strength, and elongation at break are plotted in Figure 9. An early increase of both properties at a lower NBR content can be observed when the dispersed NBR size is smaller, consistent with our previous results.

## **CONCLUSIONS**

Finer dispersion of NBR, whose AN content is 30 wt %, could be obtained in the SAN/NBR blends, when the melt viscosity of the matrix SAN was increased up to that of the NBR or the AN content of the SAN matrix was reduced in the range of 19–32 wt %, and this finer dispersion was affirmative for the higher values of impact strength and elongation at break of the SAN/NBR blends.

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