

Morphology and Physical Properties of SAN/NBR Blends: The Effect of AN Content in NBR

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ABSTRACT: Poly(styrene-*co*-acrylonitrile) (SAN), of which the content of acrylonitrile (AN) repeating unit is 32 wt % (SAN32), was blended with poly(butadiene-*co*-acrylonitrile) (NBR). The effects of AN repeating unit content in NBR on the miscibility, morphology, and physical properties of SAN32/NBR (70/30 by weight) blends were studied. Differential scanning calorimetry and the morphology observed by transmission electron microscopy showed that the miscibility between SAN32 and NBR was increased as the AN content in NBR was increased up to 50 wt %. The impact strength and some other mechanical properties of the blends had the maximum value when the AN content in NBR was 34 wt %. In the measurement of viscoelasticity at melt state, SAN32/NBR blends showed yield behavior at low shear rate, and this behavior was most evident when the AN content in NBR was 34 wt %. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 78: 1861–1868, 2000

Key words: SAN; NBR; miscibility; AN content; impact strength; DSC; TEM; viscoelasticity; mechanical properties

INTRODUCTION

The need to broaden the performance spectrum of plastics has stimulated much interest in blending different types of polymers to obtain materials having a balanced combination of specific properties.¹ The majority of commercial polymer blends are a phase-separated mixture in which the components reside in separate domains because of the positive enthalpy change and the small increase of entropy on mixing. So, the successful design of polymer blend systems requires the ability to control or manipulate the morphology of the blends that determines the physical properties of phase-separated polymer blends. The thermodynamic factor such as interfacial tension, and the rheological factors such as the viscosity and elasticity of

component polymers or compounding shear rate, can be illustrated as the factors for the optimum morphology design.^{2–7}

Toughening of brittle polymer by dispersed rubber particle is a typical example of polymer-blend application. The optimum size of dispersed rubber particle in rubber-toughened polymers depends on the chain structure of the matrix polymer.⁸ Because large rubber particles are more effective in initiating the crazing and small ones are more effective in initiating the yielding, larger particles are preferred for toughening the more brittle matrices, and smaller particles are preferred for toughening the less brittle matrices. For example, the optimum rubber diameter for toughening polystyrene was reported to be 2.5 μm , and that of poly(styrene-*co*-acrylonitrile) (SAN) was reported to be 0.75 or 0.3 μm .^{8,9}

Poly(butadiene-*co*-acrylonitrile) (NBR) is an important modifier of SAN or acrylonitrile-butadiene-styrene copolymer (ABS) to improve the

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Table I Characteristics of Polymers Used in This Study

Resin Notation	Source	Grade	AN Content (wt %)	T_g (°C)	Mooney Viscosity ^a (ML ₁₊₄)
SAN	BASF Company Ltd. (Ulsan, Korea)	—	32	107.1	—
NBR1	Nippon Zeon (Japan)	DL-401L	18	-53.4	65
NBR2	Nippon Zeon (Japan)	DN-300	28	-37.5	47
NBR3	Bayer (Germany)	K34.82	34	-27.7	82
NBR4	Nippon Zeon (Japan)	DN-101L	42	-15.8	60
NBR5	Bayer (Germany)	K50.75	50	-4.4	75

^a Measured at 100°C.

impact strength or mat surface appearance.^{10,11} Despite the commercial usefulness of these NBR/SAN or NBR/ABS blends, there are few published articles that can give systematic information about thermodynamic or rheologic factors to design optimum physical properties of these blends.^{12,13} In our previous article,¹⁴ we reported on the effect of acrylonitrile (AN) content and melt viscosity of SAN on the physical properties of SAN/NBR blends.

In random copolymer blends, the miscibility behavior and the consequent physical properties change systematically as the relative composition of constituent repeating units in the random copolymer varies.¹⁵⁻¹⁷

According to Cowie et al.,¹³ the miscibility of SAN32, SAN, the AN content of which is 32 wt %, with NBR, will increase as the AN content of NBR increases up to 50 wt %. In the present article, we report some results about the variation of physical properties in SAN32/NBR blends, according to the change of the AN content of NBR.

EXPERIMENTAL

Commercial grades of SAN and NBRs listed in Table I were used as received. Dried resins were hand-mixed thoroughly at proper compositions shown in Table II and melt-blended with a corotating twin-

screw extruder (Berstorff ZE25, $L/D = 33$) at a zone temperature profile of 190–210°C and 250 rpm. The temperature of strands extruding from die was about 200°C, and they were quenched in water and pelletized subsequently. After drying at 80°C for 3 h, it was injection-molded with Dongshin Promax 150 injection molding machine. The machine was set at the barrel temperature of 200°C and mold temperature of 50°C.

Glass transition temperature (T_g) was determined with a modulated differential scanning calorimeter (TA Instruments DSC 2910 Modulated DSC). The temperature at the half-height of the heat capacity change was taken as the transition point. All runs were carried out at a heating rate of 3.5°C/min and amplitude of $\pm 0.7^\circ\text{C}$ in modulated DSC mode with samples of about 10 mg.

Morphology was observed with a transmission electron microscope (TEM, Hitachi H-8100(II)). Thin sections were cut perpendicular to flow direction from the extrudate of melt indexer. Rubber particles were stained with a 4% OsO₄ solution for 2 h.

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

Table II Compositions (by weight) of SAN/NBR Blends

Blend Designation	SAN	NBR1	NBR2	NBR3	NBR4	NBR5
A1	70.0	30.0	—	—	—	—
A2	70.0	—	30.0	—	—	—
A3	70.0	—	—	30.0	—	—
A4	70.0	—	—	—	30.0	—
A5	70.0	—	—	—	—	30.0

Table III T_g 's and B_{blend} of SAN/NBR Blends

Blend	$T_{g,\text{SAN}}$ (°C)	$T_{g,\text{NBR}}$ (°C)	B_{blend} (J/cm ³)
A1	110.1	-54.4	3.83
A2	109.8	-37.2	2.20
A3	106.7	-27.1	1.54
A4	87.9	-16.6	0.90
A5	72.2	8.9	0.59

Surface gloss was measured using a Glossmeter (Gardner) with incident angles of 20°, 60°, and 85° according to DIN 67530.

Melt rheologic properties were measured with a parallel plate fixture of advanced rheometrics expansion systems (ARES, Rheometrics) at 220 and 240°C. The frequency sweep was done with 10% strain.

RESULTS AND DISCUSSION

Thermal Properties

To analyze the miscibility of SAN/NBR blends, T_g 's of blends were observed by differential scanning calorimetry, and the results are shown in Table III. All the blends have two separate T_g 's and this shows that these blends are phase-separated into SAN- and NBR-rich phase.

In the blends of A1, A2, and A3, two T_g 's of SAN-rich phase ($T_{g,\text{SAN}}$) and NBR-rich ($T_{g,\text{NBR}}$) appear almost at the same temperature regions of pure polymers (see Table I). However, in A4, $T_{g,\text{SAN}}$ is somewhat decreased, and in A5, both T_g 's have the values closely shifted toward each other. These results show that in A4, some amount of NBR is preferentially dissolved into SAN-rich phase, and in A5, some mutual dissolution of both SAN and NBR molecules into the other phases occurred. These results show that partial miscibility between SAN32 and NBR is enhanced as the AN content in NBR is increased up to 50 wt %.

According to the mean field approximation of miscibility in binary mixtures of random copolymers represented by $(A_x B_{1-x})_n$ and $(C_y B_{1-y})_m$, the net interaction parameter, B_{blend} , is given by

$$B_{\text{blend}} = xyB_{AC} + (1-x)yB_{BC} + x(1-y)B_{AB} - x(1-x)B_{AB} - y(1-y)B_{BC} \quad (1)$$

where B_{ij} is the interaction parameters for repeating unit i and j , and x and y are the volume

fractions of constituent repeating units in the copolymers.¹⁵ The partial miscibility increases as B_{blend} is decreased, and two polymers become miscible when B_{blend} is less than B_{crit} . Here, B_{crit} is the conformational entropy contribution and is generally <0.1 J/cm³ for high molecular weight polymers. Cowie et al. reported that interaction parameters between styrene-acrylonitrile, styrene-butadiene, and acrylonitrile-butadiene can be estimated to be 22.8, 2.7, and 34.6 J/cm³, respectively.¹³ The B_{blend} 's of our SAN/NBR blends were calculated by these values. The results in Table III show that partial miscibility between SAN 32 and NBR will be enhanced as the AN content in NBR is increased up to 50 wt %.

Morphology

Figure 1 shows the TEM photographs of SAN/NBR blends. All the blends show NBR particles dispersed in SAN matrix. However, the size of dispersed NBR particles decreases as the AN content in NBR is increased. This decreased size of rubber particles supports the enhanced partial miscibility, suggested by T_g behavior.

Wu² showed that in many polymer/rubber blends where the rubber has higher viscosity than the polymer, the number-average particle diameter, a_n , of dispersed rubber phase can be described by:

$$a_n \propto \frac{4\gamma}{G\eta_m} \left(\frac{\eta_d}{\eta_m} \right)^{0.84} \quad (2)$$

where G is the shear rate, γ the interfacial tension, η_m the matrix viscosity, and η_d the dispersed-drop viscosity.

Equation (2) shows that a_n will decrease when γ is decreased by enhanced partial miscibility, if other rheologic factors in eq. (2) do not overwhelm the effect of γ variation. So, the reduction of rubber particle size in Figure 1 at high AN content of NBR might be due to the predominant effect of γ reduction caused by enhanced partial miscibility, because γ and B_{blend} have the relation²

$$\gamma \propto B_{\text{blend}} \quad (3)$$

Mechanical Properties

In rubber-toughened polymers, the dispersed rubber phase enhances the toughness mainly by promoting the energy dissipation. Matrix crazing and rubber cavitation were reported as the major toughening mechanism of ABS.¹⁸ Because crazing is more likely to be initiated at large rubber particles

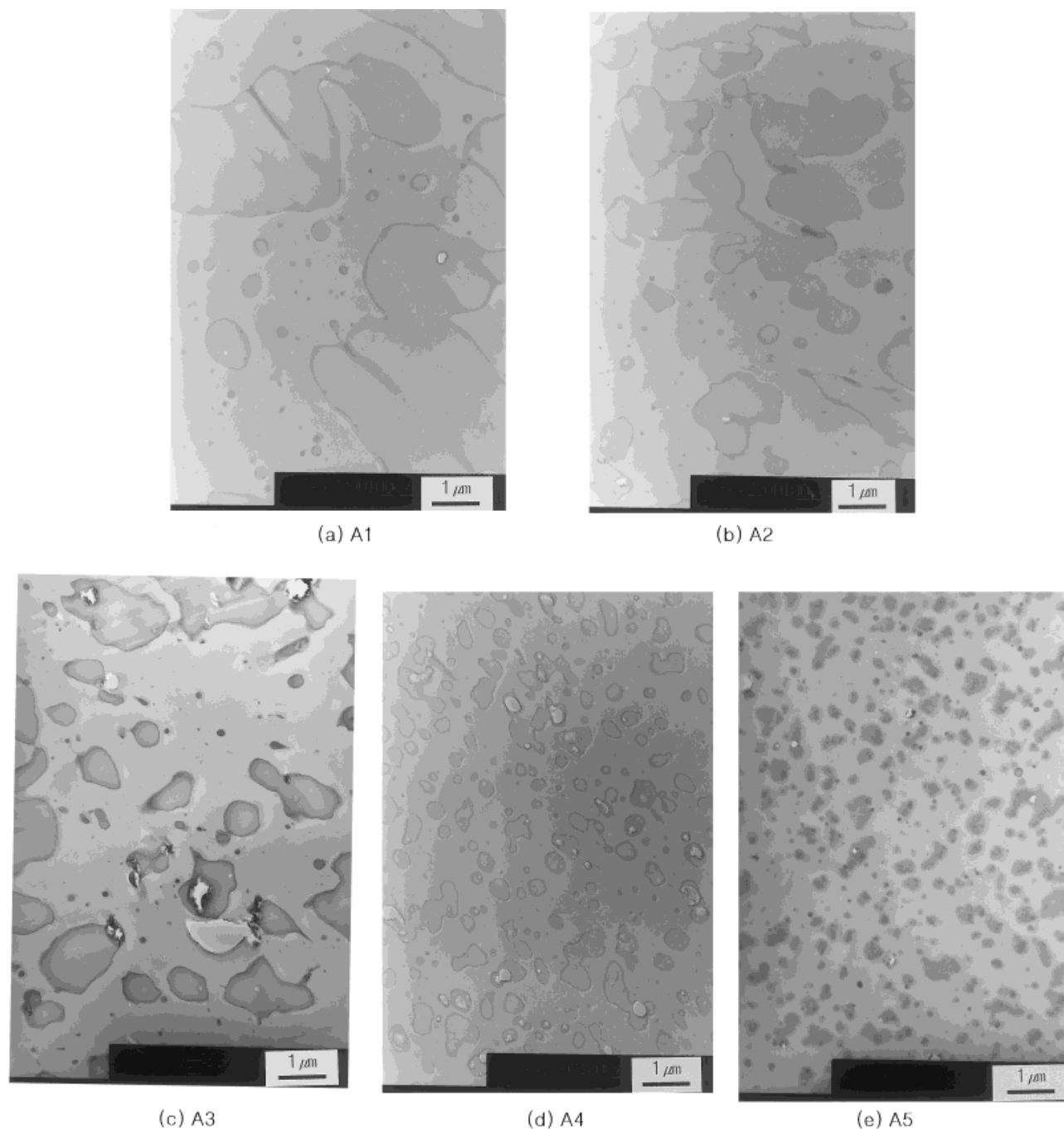


Figure 1 Transmission electron micrographs of (a) A1, (b) A2, (c) A3, (d) A4, and (e) A5.

and cavitation is more likely to occur at small rubber particles, the plot of toughness versus rubber particles size at a constant amount of rubber gives a bell-shaped curve.⁸ In SAN/rubber blend, the optimum rubber diameter was reported to be $0.3 \mu\text{m}$ when the rubber content was 15 wt %.⁹ In Table IV, we can see that both Izod and Charpy impact strengths show the maximum values in A3. These

results and Figure 1 show that the optimum average rubber diameter for toughening SAN/NBR blend is about $0.7 \mu\text{m}$. Because toughening is a complicated process where many variables can alter the optimum rubber diameter, the difference in kind or amount of rubber might be illustrated as the cause of the discrepancy of this study from previous reports^{8,9} about optimum rubber diameter.

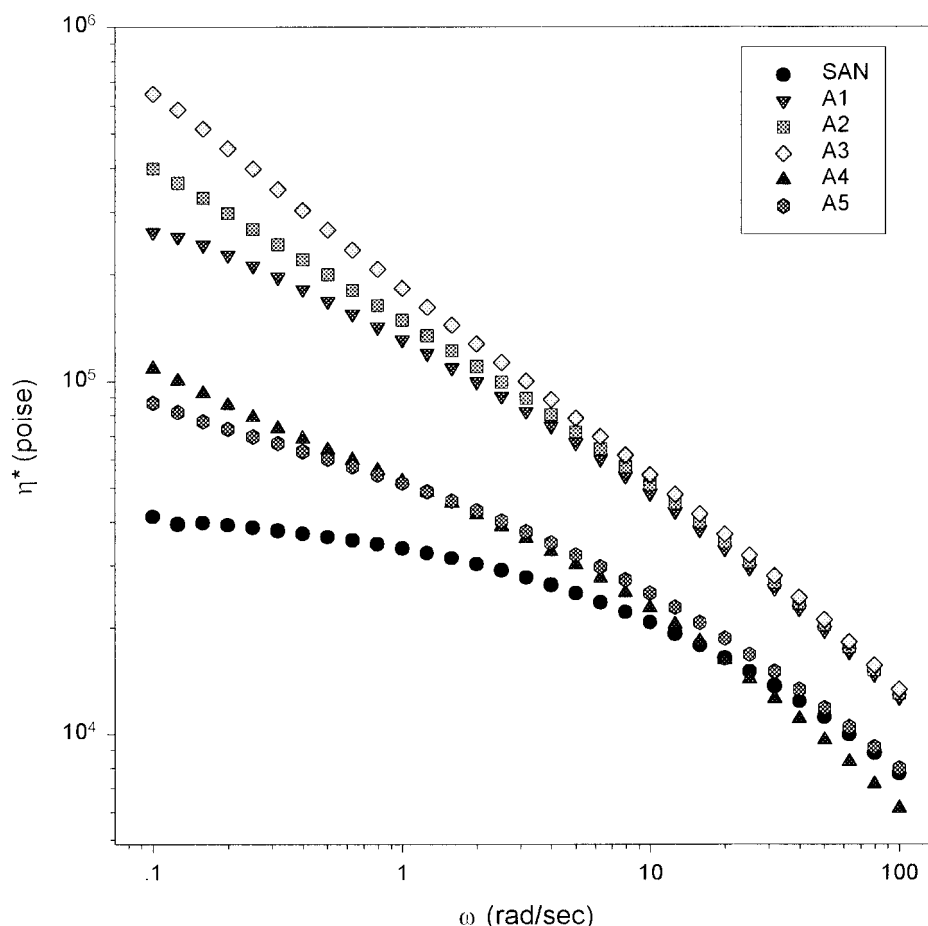
Table IV Physical Properties of SAN/NBR Blends

Blend	1/8" Izod Impact Strength (kg cm/cm)	Charpy Impact Strength (kJ/m ²)	Tensile Yield Strength (kg/cm ²)	Elongation at Break (%)	Flexural Strength (kg/cm ²)	Flexural Modulus (kg/cm ²)	Vicat Softening Temperature (°C)	Gloss		
								(20°)	(60°)	(85°)
A1	7.5	3.4	422	9.3	613	21,741	89.4	6.6	39.5	73.7
A2	14.2	5.7	424	14.6	600	20,371	88.0	13.3	46.3	83.9
A3	44.5	14.0	361	23.0	531	18,085	84.0	10.4	49.7	89.4
A4	5.9	3.3	452	24.3	670	21,513	77.6	23.3	77.9	93.9
A5	2.7	2.3	551	12.8	822	26,522	76.2	42.9	83.9	95.6

In Table IV, we can see that tensile yield strength, flexural strength, and flexural modulus all show a minimum value in A3. Finer distribution of soft rubber phase is expected to reduce these properties, whereas enhanced stiffness of NBR itself at high AN content is expected to increase these properties. So, the initial decrease of the properties according to the order A1 > A2 > A3 seems to be due to the

preferential effect of finer rubber size, and the latter increase of these properties according to the order A3 < A4 < A5 seems to stem from the preferential effect by inherent stiffness of NBR.

The decrease of Vicat-softening temperature according to the order A1 > A2 > A3 > A4 > A5 might be due to the increased partial miscibility between SAN and NBR, which reduces $T_{g,SAN}$ by

**Figure 2** Complex viscosity versus frequency for SAN and SAN/NBR blends at 220°C.

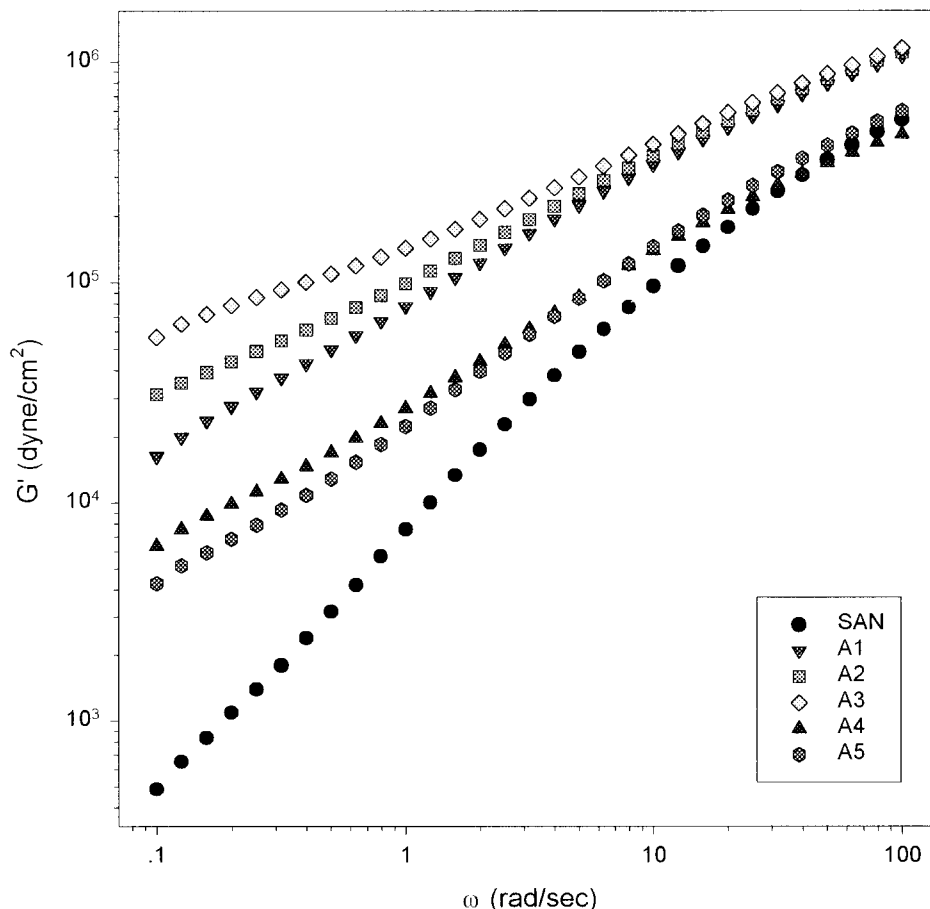


Figure 3 Storage shear modulus versus frequency for SAN and SAN/NBR blends at 220°C.

the partial dissolution of NBR molecules into SAN matrix (see Table III).

In Table IV, gloss generally increases as the size of dispersed NBR particles is reduced. Reduced scattering by small size rubber may be the cause.

Rheologic Properties

In Figure 2, we can see that SAN exhibits almost Newtonian behavior at low shear rates showing zero shear viscosity. However, SAN/NBR blends show shear thinning behavior even at low shear rate. This upturn of viscosity at low shear rate is frequently observed in heterogeneous polymer blends, and this yield behavior is explained as due to agglomeration or three-dimensional association of dispersed phase.^{19,20} In the homogeneous polymer, $\log G'$ (storage shear modulus) versus $\log \omega$, or $\log G''$ (loss shear modulus) versus $\log \omega$ plots, generally have asymptotic slope of 2 and 1, respectively, at low shear rate.²¹ However, in het-

erogeneous polymer blends such as rubber-modified polymers, the addition of rubber particles to a matrix polymer enhances both G' and G'' , and sometimes a pseudo-equilibrium value is attained at low shear rate.²¹⁻²⁴ This phenomenon is more evident in G' than in G'' .²³ In Figure 3, we can see that SAN/NBR blends have higher values of G' 's compared with simple additive values of constituent polymers (Fig. 4) at low shear rate. It was reported that this yield behavior is more evident when the three-dimensional network structure can more easily be formed and this associated structure has long relaxation time. Utracki reported that this yield behavior becomes more evident as the amount and size of dispersed phase is increased.²⁰ We observed, in our previous article,¹⁴ that in SAN/NBR blends the yield behavior was enhanced when the size of dispersed NBR droplet was increased by the lower viscosity of SAN matrix or by the reduced miscibility between SAN and NBR. However, Ahn et al. observed that

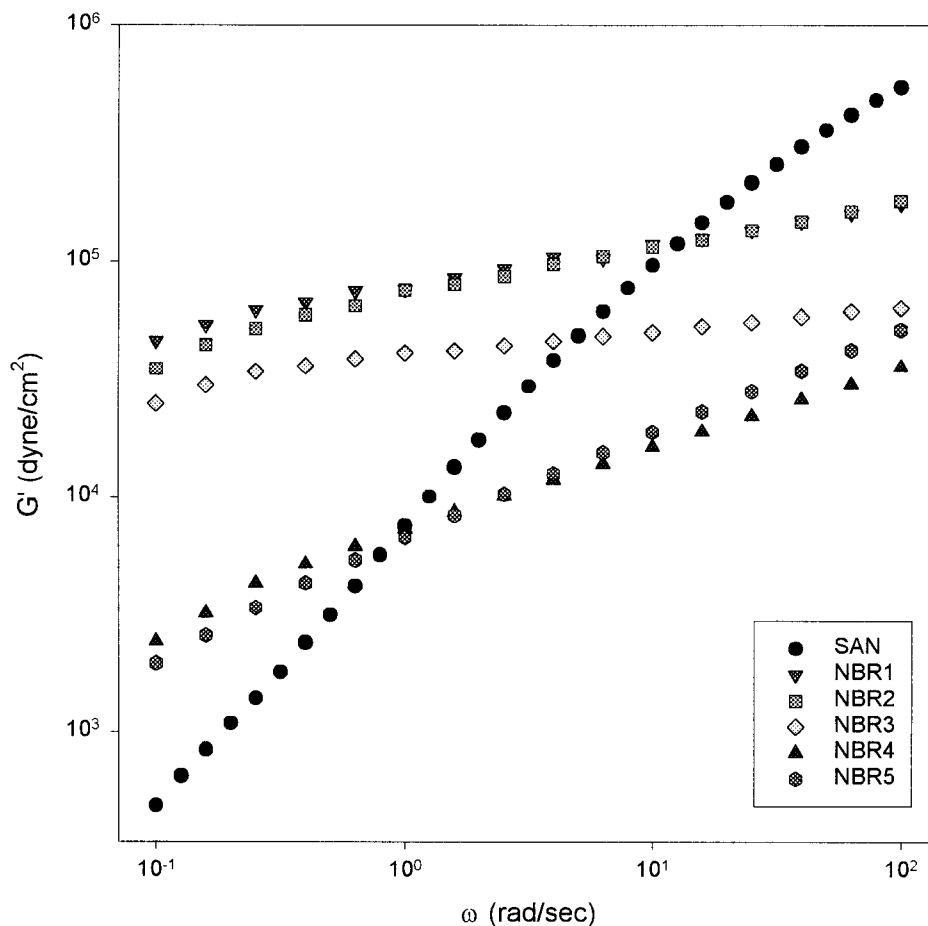


Figure 4 Storage shear modulus versus frequency for SAN and NBR's at 220°C.

yield behavior increased when some amount of compatibilizer was added in polyarylate/polystyrene blend.²⁵ This seems to be due to the fact that the deformed structure has a long relaxation time when the interfacial tension between the dispersed phase and the matrix was reduced by the added compatibilizer, although the size of dispersed phase is reduced in the presence of compatibilizer. To compare the degree of deviation of G' from the simple additive value due to yield behavior at low shear rate, we calculated the deviation by:

$$Deviation = \frac{G'_{blend} - G'_{SAN}}{(\omega_{SAN}G'_{SAN} + \omega_{NBR}G'_{NBR}) - G'_{SAN}} \quad (4)$$

where ω_i 's are the weight fractions of constituent polymers in blend, and G'_j 's are the storage shear moduli of constituent polymers and blend.

In Table V, we can see that the yield behavior at 220°C shows the first increase according to the order A1 < A2 < A3, and the next decrease ac-

ording to the order A3 > A4 > A5, as the miscibility between SAN and NBR is increased. The first increase shows that the effect of reduced interfacial tension by enhanced miscibility overwhelms the effect of reduced size of dispersed NBR phase in yield behavior. However, when the rubber particles disperse too finely, the agglomeration itself cannot easily occur, and this seems to be the cause of the second small decrease. Besides, Table III shows that the deviation is largest in A3 at 240°C also. However, in other blends the values of deviation are <1.00. This shows that in these blends too low an elasticity (G') of SAN matrix at high temperature mask the elasticity (G') of dispersed NBR phase and that due to agglomeration.

CONCLUSIONS

In SAN32/NBR (70/30 by weight) blends, we can conclude the following. The miscibility increased

Table V Deviation of G'_{blend} from Simple Additive Value

Blend	Temperature (°C)	ω (rad/sec)	Deviation
A1	220	0.10	1.15
A2	220	0.10	2.94
A3	220	0.10	15.51
A4	220	0.10	10.02
A5	220	0.10	8.55
A1	220	0.25	1.67
A2	220	0.25	3.12
A3	220	0.25	16.52
A4	220	0.25	11.17
A5	220	0.25	10.83
A1	240	0.10	0.15
A2	240	0.10	1.38
A3	240	0.10	12.23
A4	240	0.10	9.82
A5	240	0.10	7.63
A1	240	0.25	0.31
A2	240	0.25	2.57
A3	240	0.25	12.92
A4	240	0.25	10.10
A5	240	0.25	8.76

as the AN content in NBR was increased up to 50 wt %. As the miscibility between SAN and NBR was increased, the size of dispersed NBR phase and Vicat-softening temperature of the blends were decreased. The impact strengths had the largest values when the AN content in NBR was 34 wt %, whereas tensile yield strength, flexural strength, and flexural modulus had minimum values. The yield behavior of SAN/NBR blends was most evident when the AN content in NBR was 34 wt %.

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