

Thermoplastic Elastomeric Blend of Nitrile Rubber and Poly(styrene-*co*-acrylonitrile). I. Effect of Mixing Sequence and Dynamic Vulcanization on Mechanical Properties

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ABSTRACT: The effects of dynamic vulcanization and blend ratios on mechanical properties and morphology of thermoplastic elastomeric (TPE) compositions, based on blends of nitrile rubber (NBR) and poly(styrene-*co*-acrylonitrile) (SAN), were studied. The TPE composition prepared by adding a rubber-curing masterbatch to softened SAN yields higher mechanical properties than that prepared by adding curatives to the softened plastic-rubber preblend. The blends having a higher rubber-plastic ratio (60 : 40 to 80 : 20) display thermoplastic elastomeric behavior, whereas those having a higher plastic-rubber ratio (50 : 50 to 90 : 10) display the behavior of impact-resistant plastics. DSC stud-

ies revealed that NBR and SAN are thermodynamically immiscible. SEM studies of the thermoplastic elastomeric compositions show that SAN forms the matrix in which fine particles of NBR form the dispersed phase. It was further confirmed by dynamic mechanical thermal analysis. Dynamic vulcanization causes a decrease in the size of dispersed particles and improvement in mechanical properties. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 1976–1987, 2003

Key words: polymer blends; dynamic vulcanization; thermoplastic elastomers; mechanical properties

INTRODUCTION

In recent years, thermoplastic elastomers (TPEs) from rubber-plastic blends have attained great importance because of their excellent processability and rubber-like behavior at ambient temperature. Many rubber-plastic blends are reported to exhibit thermoplastic elastomeric behavior and some have been commercialized.^{1,2}

In general TPEs have heterophase morphology, whether the TPE is derived from either block copolymers or rubber-plastic blends or ionomers. Generally speaking, the hard domains soften or ionic clusters undergo dissociation at elevated temperatures, thus allowing the material to flow. When cooled, the hard domains again solidify to provide high tensile strength at normal-use temperatures. The soft domains give the material its elastomeric characteristics.³

For many end uses, the ideal rubber-plastic blend consists of finely divided elastomer particles dispersed in a relatively small amount of continuous plastic phase. The elastomer particles should be crosslinked to promote elasticity and also for the sta-

bility of the phases. The favorable morphology should remain during the fabrication of the material into parts and in use.⁴

There has been much commercial interest in dynamic vulcanization since the introduction of proprietary products (e.g., Santoprene thermoplastic elastomer) prepared by the dynamic vulcanization of blends of polyolefin rubber with polyolefin resin.⁵ If the elastomer particles of such a blend are small enough, there is improvement in blend properties such as permanent set, ultimate mechanical properties, fatigue resistance, resistance to attack by fluids, high temperature utility, stability of phase morphology in the melt, melt strength, and thermoplastic fabricability.⁶

Coran et al.^{7–10} extensively studied in detail thermoplastic elastomers from various plastic-rubber blends. They prepared TPEs by dynamic vulcanization, that is, the process of crosslinking of the rubber during its melt-mixing with molten thermoplastics. Their investigations included, for example, nitrile rubber (NBR)/polypropylene (PP) and nylon/NBR blends. Ahn et al.¹¹ dealt with the morphology and physical properties of 30 : 70 blends of NBR/poly(styrene-*co*-acrylonitrile) (SAN). They also studied the effect of acrylonitrile content and melt viscosity of SAN on the above properties. Roychoudhury and Bhowmick^{12,13} investigated the properties of NBR/PP and polycarbonate/NBR blends. Namboodiri et al.¹⁴ reported the mechanical properties and morphology of SAN/epoxidized

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TABLE I
Details of the Materials

Material	Supplier/manufacturer
NBR	
Grade: N553NS	Apar Industries Ltd., India
ACN content: 34%	
Mooney viscosity: ML_{1+4} at 100°C, 46	
SAN	
Grade: Lustron Sparkle	Monsanto, St. Louis, MO
ACN content: 27%	
MFI: 1.91 g/10 min at 200°C under a load of 2.16 kg	
Zinc oxide ^a	E-Merck, Mumbai, India
Stearic acid ^a	Local supplier
MBT ^{a,b}	ICI Ltd., Rishra, India
TMTD ^{a,c}	ICI Ltd., Rishra, India
Sulfur	Qualigens, Mumbai, India
Dicumyl peroxide (DCP) (98% pure)	Aldrich, Milwaukee, WI
Methyl ethyl ketone (98% pure)	E-Merck, Mumbai, India

^a Rubber grade.

^b Mercaptobenzothiazole.

^c Tetramethyl thiuram disulfide.

natural rubber (ENR) blends. Kalfoglou¹⁵ studied the properties of nylon-6/SAN blends. Mehrabzadeh and Delfan¹⁶ used various systems for the dynamic crosslinking of thermoplastic elastomers based on nylon-6/NBR blends and studied their effect on morphology and mechanical properties of the resulting thermoplastic elastomer.

Even though many TPEs are commercially available, development of specialty TPEs with oil-resistance characteristics have not received wide attention.

The present investigation reports the results of studies on the development and properties of thermoplastic elastomeric compositions of NBR/SAN blends, with and without dynamic vulcanization.

EXPERIMENTAL

Materials

Details of the materials are given in Table I.

TABLE II
Compositions of the 60/40, 70/30, and 80/20 NBR/SAN Blends with Different Level of Curing Systems^a

Ingredient	NBR	SAN	Zinc oxide	Stearic acid	MBT	TMTD	Sulfur	DCP
B ₆	60	40	—	—	—	—	—	—
B ₆ S _{0.25}	60	40	3	2	1	0.5	0.25	—
B ₆ S _{0.5}	60	40	3	2	1	0.5	0.5	—
B ₆ S _{0.75}	60	40	3	2	1	0.5	0.75	—
B ₆ S _{1.0}	60	40	3	2	1	0.5	1.0	—
B ₆ P _{0.5}	60	40	—	—	—	—	—	0.5
B ₆ P _{1.0}	60	40	—	—	—	—	—	1.0
B ₇	70	30	—	—	—	—	—	—
B ₇ S _{0.25}	70	30	3	2	1	0.5	0.25	—
B ₇ S _{0.5}	70	30	3	2	1	0.5	0.5	—
B ₇ S _{0.75}	70	30	3	2	1	0.5	0.75	—
B ₇ S _{1.0}	70	30	3	2	1	0.5	1.0	—
B ₇ P _{0.5}	70	30	—	—	—	—	—	0.5
B ₇ P _{1.0}	70	30	—	—	—	—	—	1.0
B ₈	80	20	—	—	—	—	—	—
B ₈ S _{0.25}	80	20	3	2	1	0.5	0.25	—
B ₈ S _{0.5}	80	20	3	2	1	0.5	0.5	—
B ₈ S _{0.75}	80	20	3	2	1	0.5	0.75	—
B ₈ S _{1.0}	80	20	3	2	1	0.5	1.0	—
B ₈ P _{0.5}	80	20	—	—	—	—	—	0.5
B ₈ P _{1.0}	80	20	—	—	—	—	—	1.0

^a Concentration of curatives are in phr, based on the NBR phase.

TABLE III
Composition of the NBR/SAN Blends^a

Ingredient	B ₀	B ₁	B ₂	B ₃	B ₄	B ₅	B ₆	B ₇	B ₈	B ₁₀
NBR	0	10	20	30	40	50	60	70	80	100
SAN	100	90	80	70	60	50	40	30	20	0

^a Parts by weight.

Preparation of the blends

The blends were prepared by mixing NBR and SAN in an internal mixer (Brabender Plasticorder PLE 330, Germany) at 180°C and 60 rpm with cam-type rotors. After mixing, the blends were removed in the hot condition and sheeted out in a water-cooled two-roll mill (Schwabenthan, Germany) at 25°C. Sheeted-out blends were compression molded between polyester sheets at 210°C in a hydraulic press (Moore Press, Birmingham, UK) at a pressure of 5 MPa for 2 min, after which the platens were cooled under pressure.

Optimization of mixing schedule

The mixing was done according to three different schemes to optimize the mixing schedule. In all the mixing cycles, the total mixing time was maintained as 6 min and the plastographs were recorded. A 70/30 (w/w) blend of NBR/SAN [curing system (in phr, based on the NBR phase): zinc oxide, 3; stearic acid, 2; MBT, 1; TMTD, 0.5; sulfur, 0.75] was used in this study and the mechanical properties were studied.

Scheme 1

NBR was taken in a Brabender Plasticorder at 70°C. Sulfur, zinc oxide, and stearic acid were added. Mix-

ing was done at 60 rpm for 4 min. The rubber compound was passed through a two-roll mill. MBT and TMTD were added and mixed. SAN was softened in the Brabender Plasticorder at 180°C for 2 min. The rubber masterbatch was added to the softened SAN and mixed at 60 rpm for 4 min (by which time, the torque stabilized). The mixture was sheeted out in a cold two-roll mill and cut into strips, which were remixed for 2 min in the Brabender Plasticorder and sheeted out.

Scheme 2

SAN was softened in the Brabender Plasticorder at 180°C for 2 min. Strips of NBR were added and mixed at 60 rpm for 1 min. Zinc oxide, stearic acid, and MBT/TMTD were added first after which sulfur was added. Mixing was continued for 3 min. The mixture was sheeted out and remixed as described earlier.

Scheme 3

Mixing was done as described in Scheme 2 but the mixing time was extended by 2 min (i.e., for a total time of 8 min). The mixture was sheeted out and remixed as described earlier.

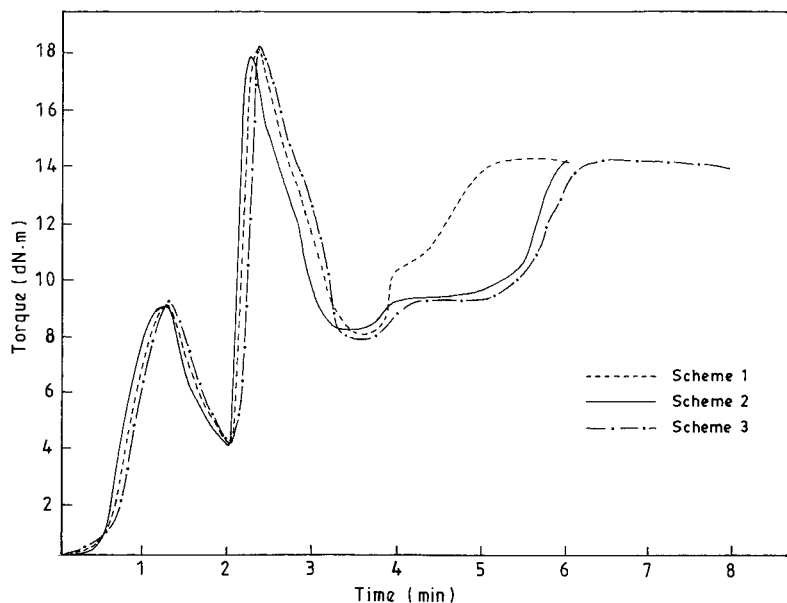


Figure 1 Brabender plastographs for the preparation of the blend B₇S_{0.75} according to mixing schemes 1, 2, and 3.

TABLE IV
Mechanical Properties of the Blend B₇S_{0.75} Prepared by Different Schemes of Blending

Scheme no.	Tensile strength (MPa)	Elongation at break (%)	Modulus at 100% elongation (MPa)	Modulus at 200% elongation (MPa)	Tension set at 100% elongation (%)
1	11.9	267	6.7	9.6	24
2	8.8	250	5.4	7.8	20
3	6.5	190	5.7	—	32

Optimization of thermoplastic elastomeric composition

Because our objective was to prepare thermoplastic elastomeric composition from NBR/SAN blends, we chose 60/40, 70/30, and 80/20 NBR/SAN blends for our study. Two different cure systems were used for dynamic vulcanization of the blends: dicumyl peroxide (DCP) and sulfur/MBT/TMTD/zinc oxide/stearic acid systems. To find the optimum dose of the curing agents, the blends were dynamically vulcanized with varying doses of the curing systems. The formulations are given in Table II. To estimate the crosslink density of the rubber phase in the blend, neat rubber vulcanizates (without SAN) were prepared, using formulations similar to those used in dynamic vulcanization. The crosslink density was determined from equilibrium swelling measurements in methyl ethyl ketone, and the Flory–Rehner equation was used to calculate the crosslink density values⁸:

$$v = \{V_p + \chi V_p^2 + \ln(1 - V_p)\} / \rho_r V_0 (V_p^{1/3} - V_p/2) \quad (1)$$

where v is the effective number of moles of crosslinked chains per gram of polymer (crosslink density), V_p is the volume fraction of polymer in the swollen mass, V_0 is the molar volume of the solvent, χ is the polymer–solvent interaction parameter, and ρ_r is the density of the polymer.

$$V_p = (D_s - F_f A_w) \rho_r^{-1} / \{(D_s - F_f A_w) \rho_r^{-1} + A_s \rho_s^{-1}\} \quad (2)$$

where D_s is the deswollen weight of the sample, F_f is the insoluble fraction, A_w is the sample weight, A_s is the weight of the adsorbed solvent corrected for swelling increment, and ρ_s is the density of solvent.

Effect of blend ratio

To determine the effect of blend ratio on the properties of the blends, the blends were prepared in all the blend ratios. Compositions of the blends are given in Table III. For study of the effect of dynamic vulcanization on blend properties, dynamically vulcanized blends were also prepared in the same blend ratios. For dynamic vulcanization, the following system was used (in phr, based on the rubber phase): zinc oxide, 3; stearic acid, 2; sulfur, 0.75; MBT, 1; TMTD, 0.5. This system was chosen on the basis of the optimization studies.

Mechanical properties of the blends

Dumbbell-shape specimens were prepared from the sheeted-out blends by compression molding. Tensile testing was done in a Zwick 1445 UTM (Germany) at a crosshead speed of 500 mm/min at 25°C. Testing was done according to ASTM D 418-98a. Young's modulus (E) was determined from the slope of the stress–strain curve in the linear region of the curve. The Shore A hardness of each composition was obtained by ASTM test method D2240-98T. Tension set

TABLE V
Mechanical Properties of NBR/SAN Blends^a

Blend designation	Tensile strength (MPa)	Elongation at break (%)	Young's modulus (MPa)	Tension set at 100% elongation (%)	Work to break (J m ⁻²)	Hardness (Shore A)
B ₀	45.8	13	364	— ^b	1139	88
B ₁	50.7 (45.5)	19 (13)	355 (224)	— ^b	1532 (1067)	94 (87)
B ₂	33.8 (39.6)	17 (17)	168 (238)	— ^b	936 (1285)	84 (81)
B ₃	31.2 (27.8)	15 (16)	280 (202)	— ^b	761 (3632)	89 (70)
B ₄	24.0 (21.0)	120 (138)	54 (81)	76 (64)	2206 (5225)	87 (90)
B ₅	15.0 (17.4)	173 (214)	25 (30)	56 (48)	2024 (8230)	82 (84)
B ₆	6.2 (14.7)	150 (265)	9 (22)	50 (45)	1231 (6883)	64 (89)
B ₇	2.2 (11.9)	196 (267)	3 (20)	44 (24)	1900 (8464)	38 (79)
B ₈	1.5 (7.2)	280 (350)	2 (12)	16 (8)	2700 (6553)	25 (66)
B ₁₀	2.1	395	1	2	2259	38

^a Values in parentheses correspond to the blends dynamically vulcanized with sulfur/MBT/TMTD system (0.75/1.0/0.5 phr).

^b Values could not be determined.

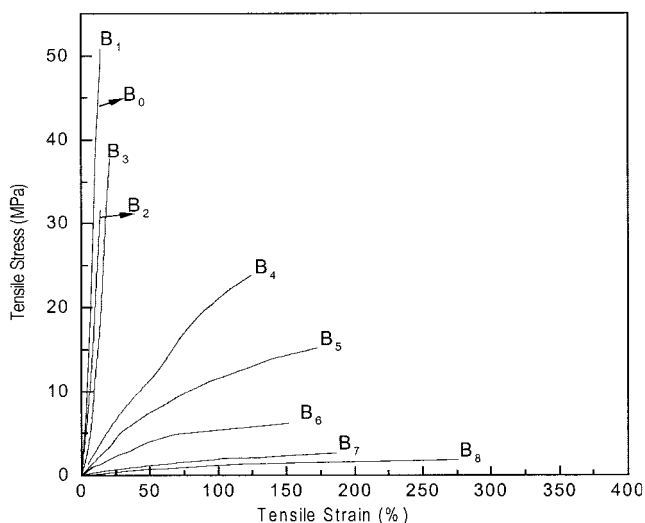


Figure 2 Tensile stress-strain curves of unvulcanized NBR/SAN blends.

was determined with dumbbell-shape specimens by ASTM D 412-98a. Toughness was calculated from the area under the stress-strain curve.

Morphology of the blends

The rubber phase in the cryofractured samples was selectively etched out by chromic acid treatment at 100°C for 1 h followed by washing with distilled water several times to remove the acid. The samples were then dried to remove traces of water. The morphology was examined under a scanning electron microscope (JSM 5800; JEOL, Peabody, MA) after gold sputtering of the samples.

Differential scanning calorimetry (DSC)

DSC studies were carried out using a thermal analyzer (Du Pont thermal analyzer, model 910; Boston, MA). The scans were taken in the temperature range from -100 to 200°C with a programmed heating rate of 20°C/min.

Dynamic mechanical thermal analysis (DMTA)

The dynamic mechanical spectra of the blends were obtained by using a dynamic mechanical thermal analyzer (DMTA IV; Rheometric Scientific, Poole, UK). The sample specimens were analyzed in tensile mode at a constant frequency of 1 Hz, strain of 0.01%, and temperature ranging from -60 to 150°C with a heating rate of 2°C/min. RSI Orchestrator software was used for data acquisition through an ACER computer. The temperature corresponding to the peak in $\tan \delta$ versus temperature plot was taken as the glass-to-rubber transition temperature (T_g).

RESULTS AND DISCUSSION

Optimization of mixing schedule

The Brabender plastographs of the three different mixing schemes for $B_7S_{0.75}$ are given in Figure 1. The torque reaches a high value and stabilizes within the total mixing time of 6 min for Scheme 1. The torque still continues to rise, even after 6 min, for Scheme 2. For Scheme 3, the torque stabilizes after an additional 2 min, as shown in Figure 1. The mechanical properties of the blends prepared by these three schemes are given in Table IV. The mechanical properties are optimum for the blend prepared by Scheme 1, given that the crosslinking reaction is nearly complete. However, in the case of Scheme 2, the crosslinking reaction is not complete; thus, the mechanical properties of the blend prepared by Scheme 2 are inferior to those of the blend prepared by Scheme 1. In the case of Scheme 3, even though the crosslinking reaction is complete, the mechanical properties are still lower. Thus, the blends for further studies were prepared according to Scheme 1.

Effect of blend ratio

Mechanical properties such as tensile strength, elongation at break, Young's modulus, tension set, toughness, and hardness for NBR/SAN blends prepared in different ratios are summarized in Table V. The tensile stress-strain curves of the samples are shown in Figure 2. As expected, the tensile strength, tension set, and hardness increase, whereas the elongation at break decreases with increase in plastic content of the blend. It is also evident that the Young's modulus decreases regularly with increasing rubber content, with a sudden drop for the B_4 composition. At higher

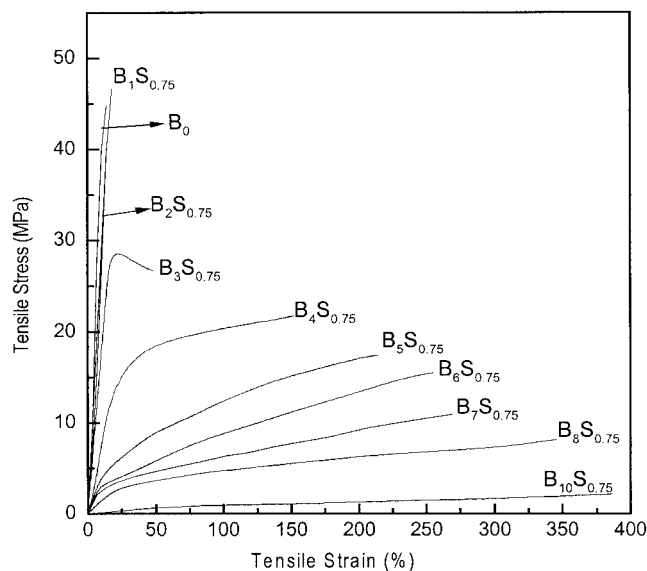


Figure 3 Tensile stress-strain curves of dynamically vulcanized NBR/SAN blends.

TABLE VI
Mechanical Properties of 60/40, 70/30 and 80/20 NBR/SAN blends dynamically vulcanized at different sulfur levels, but at constant MBT (1 phr), TMTD (0.5 phr) levels.

Blend designation	Tensile strength (MPa)	Elongation at break, (%)	Modulus at 100% elongation (MPa)	Modulus at 200% elongation (MPa)	Tension set at 100% elongation (%)	Hardness (Shore A)
B ₆	6.2	150	5.3	—	50	64
B ₆ S _{0.25}	8.8	135	8.5	—	48	91
B ₆ S _{0.50}	11.9	213	9.4	11.7	46	89
B ₆ S _{0.75}	14.5	264	10.2	13.2	45	89
B ₆ S _{1.0}	14.6	199	11.6	—	47	90
B ₇	2.2	191	2.1	—	44	38
B ₇ S _{0.25}	7.5	246	5.8	7.3	32	83
B ₇ S _{0.50}	9.5	268	6.2	8.6	24	81
B ₇ S _{0.75}	11.9	267	6.7	9.6	24	79
B ₇ S _{1.0}	13.4	243	8.3	12.1	28	81
B ₈	1.5	280	1.3	1.4	16	25
B ₈ S _{0.25}	5.1	352	2.6	3.8	10	59
B ₈ S _{0.50}	6.6	345	3.0	4.6	8	61
B ₈ S _{0.75}	7.3	350	3.3	5.0	8	66
B ₈ S _{1.0}	9.3	360	3.8	5.9	10	66

plastic-rubber ratios, the blends display behavior of impact-resistant plastics and at higher rubber-plastic ratios, the behavior resembles that of rubbery materials. In the range of compositions B₆-B₈, the elongation at break is high and the tension set is low. Hence, the compositions B₆, B₇, and B₈ were chosen for further investigations.

Unvulcanized versus dynamically vulcanized blends

The mechanical properties of the dynamically vulcanized blends are given in parentheses in Table V and the tensile stress-strain curves are shown in Figure 3. Tensile strength is not greatly affected by dynamic vulcanization for formulations B₁ to B₅. However, tensile strength, elongation at break, Young's modulus, hardness, and tension set at 100% elongation are improved after dynamic vulcanization for B₆, B₇, and B₈. The blends B₁, B₂, and B₃ show brittle behavior, which is scarcely affected by the presence of the rubber phase and its dynamic vulcanization. The blends B₄, B₅, B₆, B₇, and B₈ show elastomeric behavior. Young's modulus, tension set, and hardness of the blends B₄, B₅, B₆, B₇, and B₈ are improved after dynamic vulcanization. However, the effect is less pronounced in the case of B₄ and B₅. In general, it can be concluded that the effect of dynamic vulcanization becomes significant only in the case of the blends with high rubber-plastic ratios, as in the case of B₆, B₇, and B₈.

Influence of concentration and nature of dynamic vulcanizing agent

The mechanical properties of the blends B₆, B₇, and B₈, which were dynamically vulcanized with varying levels of sulfur, are given in Table VI (the dosage of other

curatives is maintained at a constant level). With an increase in the concentration of the vulcanizing agent, the tensile strength and modulus at 100% elongation increase because of the crosslinking of the rubber phase, which helps in dissipation of the large amount of energy. The elongation at break increases up to a certain network density of rubber and the tension set decreases, especially at high rubber content. The crosslink density of the rubber phase was also determined and the variation of mechanical properties with crosslink density of the rubber phase is shown in Figure 4 for a representative blend (70/30 w/w NBR/SAN). A similar trend was also observed for the other blend ratios. It may be noted that the relative increase in properties (tensile strength, modulus, hardness,

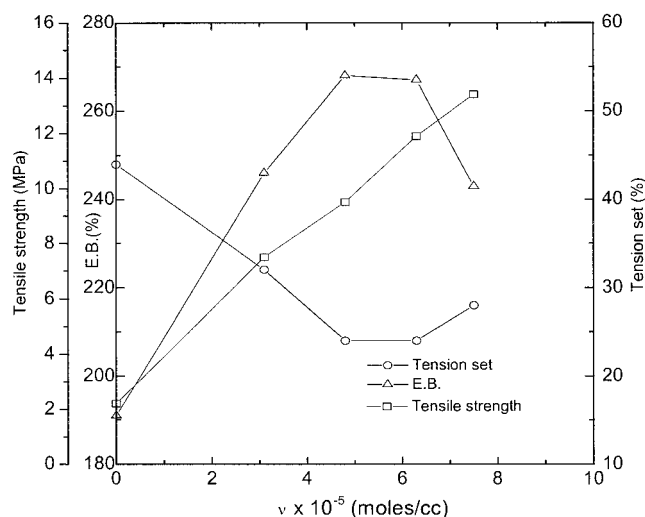


Figure 4 Effect of crosslink density of the NBR phase on the physical properties of 70/30 NBR/SAN blends dynamically vulcanized with sulfur system.

TABLE VII
Mechanical Properties of 60/40, 70/30, and 80/20 Blends of NBR/SAN Dynamically Vulcanized with Different Amounts of Dicumyl Peroxide

Blend designation	Tensile strength (MPa)	Elongation at break (%)	Modulus at 100% elongation (MPa)	Tension set at 100% elongation (%)	Hardness (Shore A)
B ₆	6.2	150	5.4	50	64
B ₆ P _{0.5}	12.9	124	12.5	64	86
B ₆ P _{1.0}	11.5	71	—	—	90
B ₇	2.2	191	2.1	44	38
B ₇ P _{0.5}	10.4	181	8.3	35	78
B ₇ P _{1.0}	9.0	67	—	—	84
B ₈	1.5	280	1.3	16	25
B ₈ P _{0.5}	5.2	185	4.3	10	60
B ₈ P _{1.0}	8.4	181	6.0	14	68

etc.) is not commensurate with the large increase in crosslink density, presumably because of the plastic phase forming the continuous matrix, as shown later. The mechanical properties of the blend B₇ (70/30, NBR/SAN) dynamically vulcanized with 0.75 and 1.0 phr of sulfur, respectively, are typical of a thermoplastic elastomer. However, the formulation with 1 phr of sulfur was difficult to process. Therefore, 0.75 phr of sulfur was chosen for further studies.

The properties of the blends B₆, B₇, and B₈, which were dynamically vulcanized with varying levels of

DCP, are given in Table VII. Among the dynamically vulcanized blends, the 80/20 (w/w NBR/SAN) blends dynamically vulcanized with 0.5 and 1.0 phr of DCP (B₈P_{0.5} and B₈P_{1.0}, respectively) show typical thermoplastic elastomeric behavior. In general, the properties of the sulfur crosslinking system are superior, presumably because of slower rate of crosslinking of the latter (Fig. 5).

Because the blend B₇S_{0.75} shows mechanical properties superior to those of the blend B₈P_{1.0}, the composition of B₇S_{0.75} was taken as the optimum composition

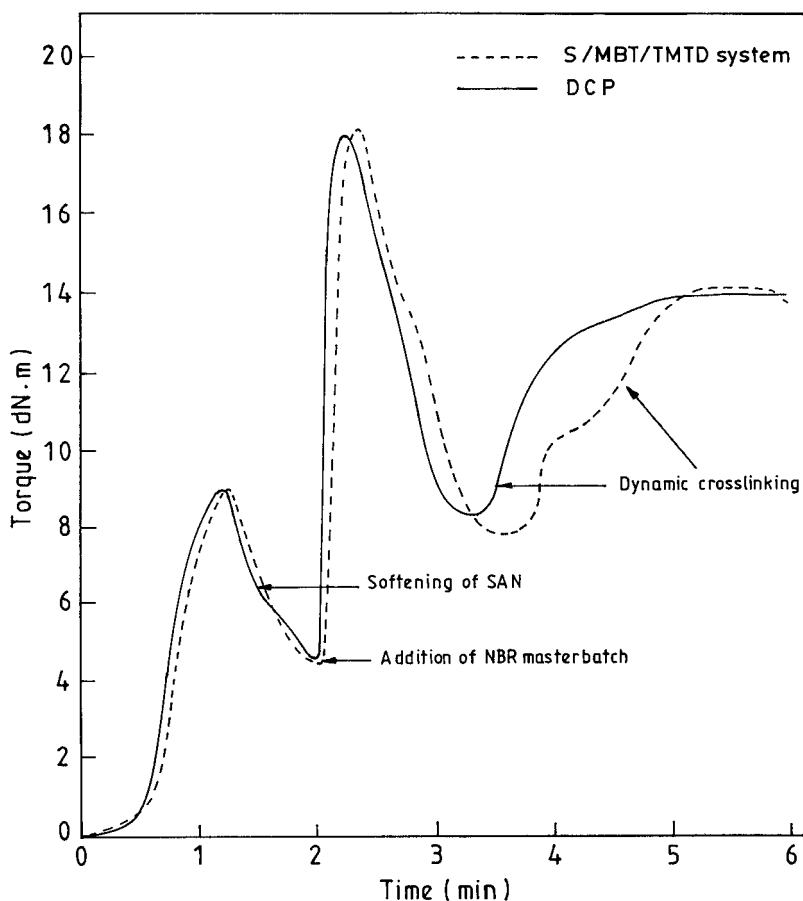


Figure 5 Brabender plastographs of the blends B₇P_{1.0} and B₇S_{1.0}.

TABLE VIII
Reprocessability of the Thermoplastic Elastomeric 70/30 NBR/SAN Blend ($B_7S_{0.75}$)

Mechanical property	Cycle I	Cycle II	Cycle III
Tensile strength, MPa	11.9	9.7	8.8
Elongation at break, %	267	266	245
Modulus at 100% elongation, MPa	6.7	5.8	5.7
Modulus at 200% elongation, MPa	9.6	8.0	6.4
Tension set at 100% elongation, %	24	22	20
Tear strength, kN m^{-1}	60.9	59.0	58.4
Toughness, J m^{-2}	8464	7744	6663
Hysteresis loss, $\text{J m}^{-2} \times 10^{-6}$	0.11	0.11	0.11

tion of thermoplastic elastomeric blend obtainable from NBR/SAN.

Reprocessability of TPE composition

To test for reprocessability, the mechanical properties of the blend $B_7S_{0.75}$ were studied after three cycles of remixing and remolding (Table VIII). The changes in properties were within acceptable limits ($\pm 10\%$) and the blend was thus considered reprocessable.

Morphology of NBR/SAN blend

The morphology of the blends B_6 and B_7 , with and without dynamic crosslinking, was studied and the

representative SEM photomicrographs are given in Figure 6(a)–(d). The blend B_6 has SAN as the matrix phase and NBR as the dispersed phase [Fig. 6(a)]. The same morphology is also retained after dynamic vulcanization [Fig. 6(b)]. In the case of B_7 , however, it can be seen that before dynamic vulcanization both rubber and plastic phases are cocontinuous [Fig. 6(c)], but after dynamic vulcanization the plastic is the continuous phase and the rubber is the dispersed phase [Fig. 6(d)]. The blend $B_7S_{0.75}$ possesses typical thermoplastic elastomeric morphology that gives the desirable mechanical properties as well as reprocessability.

The DSC results of typical NBR/SAN blends B_0 , B_7 , $B_7S_{0.75}$, and B_{10} along with a dynamically vulcanized blend, are given in Table IX and the representative

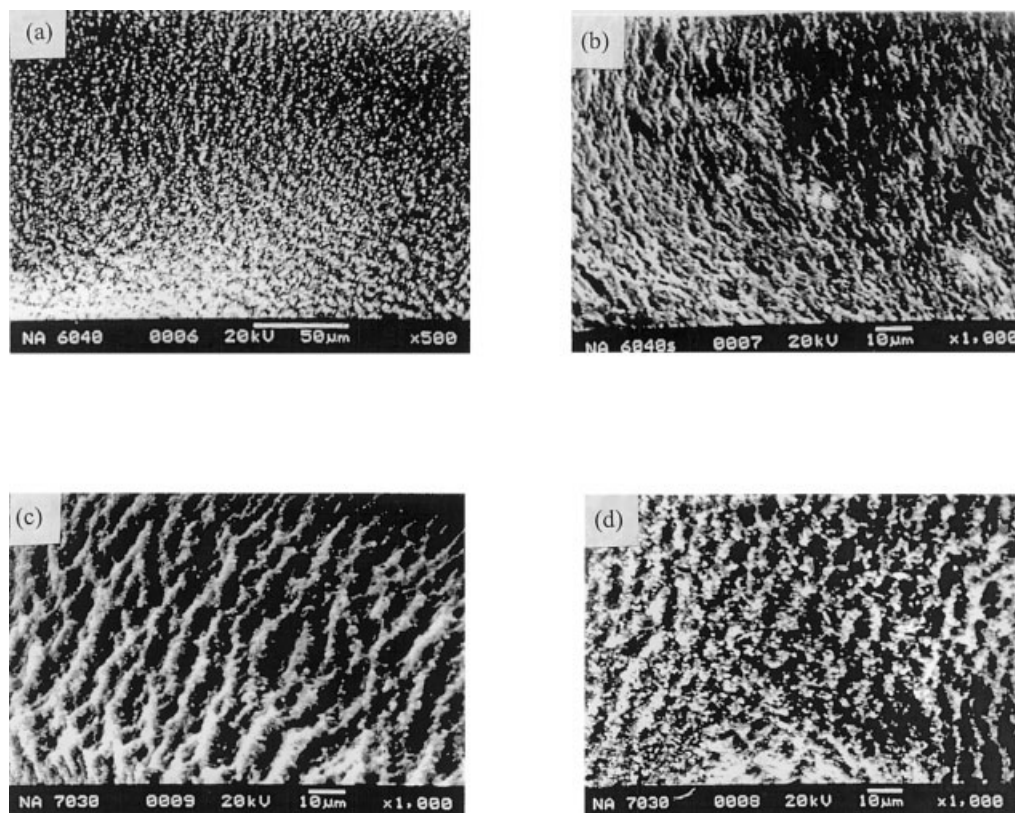


Figure 6 Morphology of the blends: (a) 60/40 NBR/SAN blend without dynamic vulcanization; (b) 60/40 NBR/SAN blend with dynamic vulcanization; (c) 70/30 NBR/SAN blend without dynamic vulcanization; (d) 70/30 NBR/SAN blend with dynamic vulcanization.

TABLE IX
DSC Results of the NBR/SAN Blends

Blend designation	Transition 1 T_g (°C)	Transition 2 T_g (°C)
B ₀	—	104
B ₇	-32	104
B ₇ S _{0.75}	-22	100
B ₁₀	-37	—

curves are shown in Figure 7. The blends show two transitions corresponding to the rubber phase and the plastic phase, indicating that the blend components are immiscible.

Expectedly, the dynamic mechanical spectra of the blends B₆, B₇, and B₈ and their dynamically vulcanized counterparts (Figs. 8 and 9) substantiate the DSC results. The changes observed because of crosslinking are reflected in the $\tan \delta$ peaks, that is, the broadening of the loss tangent peak of the rubber phase with a reduction in the peak height. The broadening of the $\tan \delta$ peak is also found to occur in all the blends. This can be explained by the fact that, in the case of unvulcanized blends, the spectra arise because of the multiple relaxations of the loosely connected or unconnected polymeric chains. Dynamic vulcanization reduces the number of relaxations. Such an observation was previously made for a variety of rubbers.¹⁷

The storage modulus of the blends at 25°C, which represents the relative stiffness of the materials at room temperature, increases with an increase in the plastic content of the blends (Table X). The E' values decrease with an increase in the NBR content of the

blends because SAN has a higher modulus value than that of NBR. The E' values of the dynamically vulcanized blends are higher than those of the unvulcanized blends because the modulus of the NBR phase is highly increased as a result of the introduction of crosslinks.

The storage moduli of the blends at 25°C (a temperature between the two T_g values of the components) as well as the theoretical values of modulus of the blends are plotted in Figure 10. The theoretical values were calculated by use of the (i) parallel model, (ii) series model, and (iii) Kerner's model.^{18,19}

In mixtures of two polymers, the phase morphology can be such that the hard phase can be continuous, the soft phase continuous, or both phases co-continuous. The modulus of the mixture must be between the parallel model upper bound M_U and the series model lower bound M_L , given by

$$M_U = \phi_H M_H + \phi_S M_S \quad (3)$$

and

$$M_L = (\phi_H/M_H + \phi_S/M_S)^{-1} \quad (4)$$

where M_H and M_S are the moduli of the pure hard and soft phases, respectively, and ϕ_H and ϕ_S are the volume fractions of the hard and soft phases, respectively.

Kerner's equation for a binary blend (i.e., one component dispersed in a matrix material) is

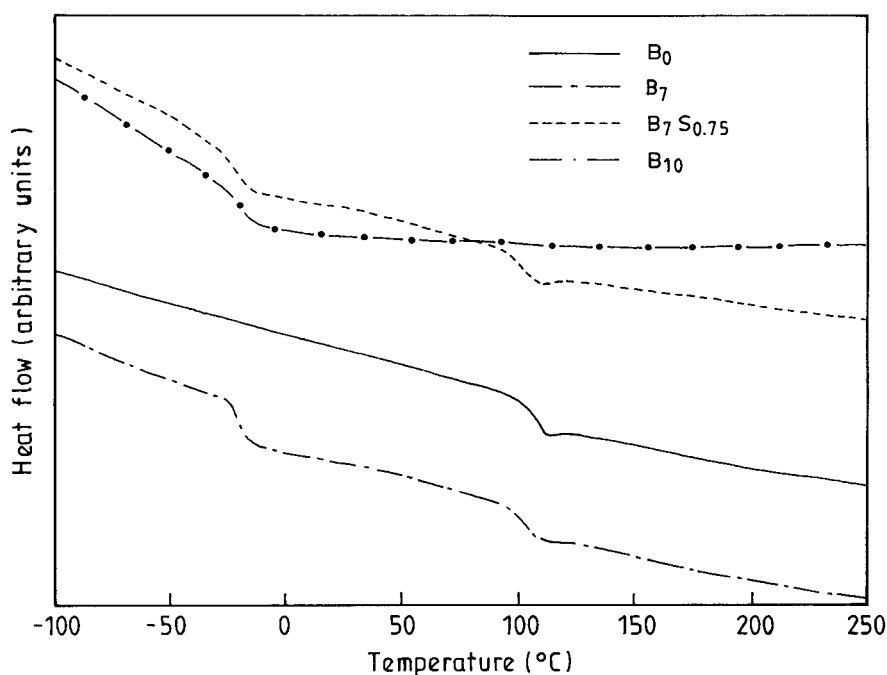


Figure 7 DSC thermograms of NBR/SAN blends.

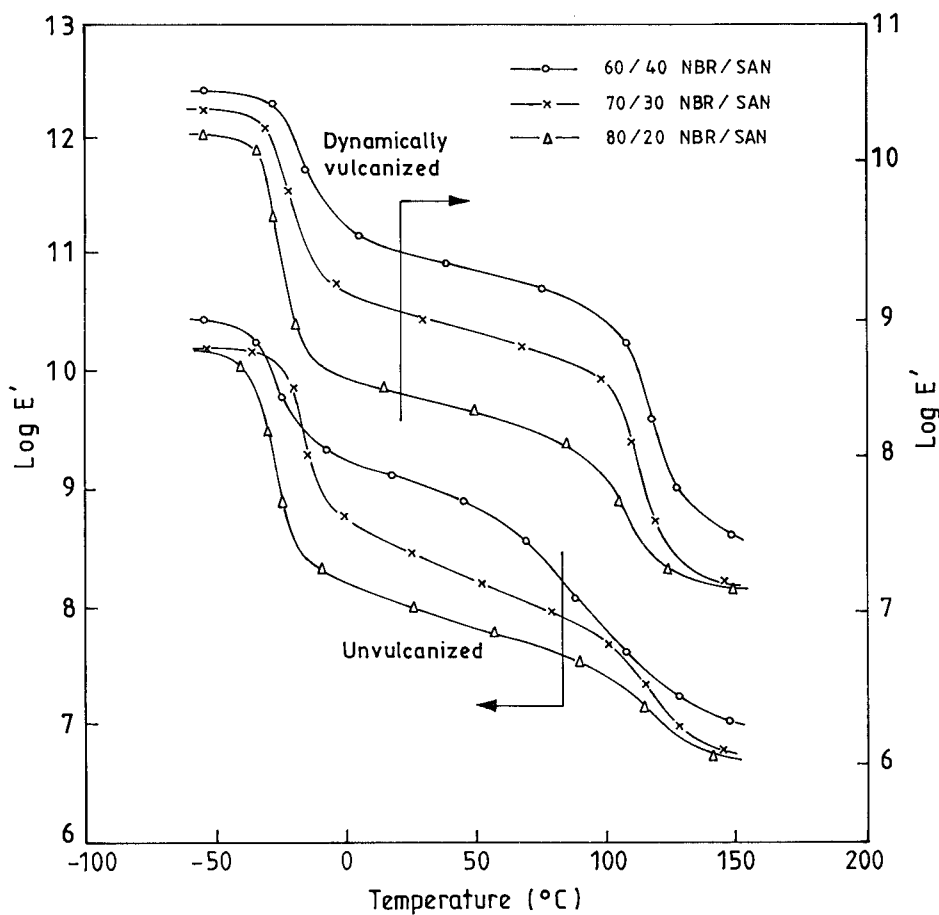


Figure 8 Dynamic mechanical spectra of NBR/SAN blends. Log E' versus temperature plot.

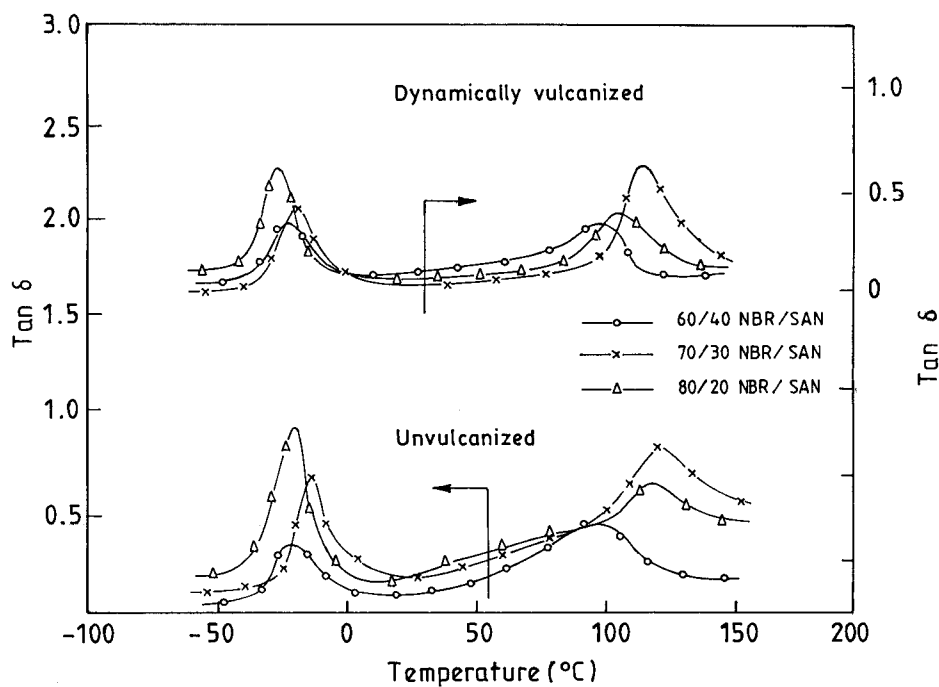


Figure 9 Dynamic mechanical spectra of NBR/SAN blends. Tan δ versus temperature plot.

TABLE X
DMTA Data of the NBR/SAN Blends

Blend designation	Transition 1			Transition 2			E' (dyn/cm ²) at 25°C
	T_g (°C)	$\tan \delta$	E' (dyn/cm ²)	T_g (°C)	$\tan \delta$	E' (dyn/cm ²)	
B ₆	-21	0.37	7.2×10^9	95	0.47	8.2×10^8	1.18×10^9
B ₆ S _{0.75}	-23	0.25	2.1×10^{10}	94	0.34	1.2×10^9	2.22×10^9
B ₇	-14	0.68	8.8×10^8	120	0.85	3.0×10^8	2.61×10^8
B ₇ S _{0.75}	-17	0.44	5.1×10^9	115	0.67	3.9×10^8	9.61×10^8
B ₈	-21	0.97	9.6×10^8	118	0.67	9.1×10^7	1.06×10^8
B ₈ S _{0.75}	-24	0.62	2.3×10^9	107	0.43	1.2×10^8	2.81×10^8

$$\frac{E}{E_m} = \gamma \frac{(1 - \phi_i)E_m + \beta(\alpha + \phi_i)E_i}{(1 + \alpha\phi_i)E_m + \alpha\beta(1 - \phi_i)E_i} \quad (5)$$

where $\alpha = 2(4 - 5\mu_m)/(7 - 5\mu_m)$, $\beta = (1 + \mu_m)/(1 + \mu_i)$, $\gamma = (1 + \mu_i)/(1 + \mu_m)$, E is the dynamic Young's modulus of the blend, E_m is the dynamic Young's modulus of the matrix material, E_i is the dynamic Young's modulus of the dispersed phase, ϕ_i is the volume fraction of the dispersed phase, μ_m is the Poisson ratio of the matrix material, and μ_i is the Poisson ratio of the dispersed phase material.

Kerner's equation has been found to represent dynamic data reasonably well for a variety of systems of the soft inclusion/hard matrix type.²⁰

It is clear from Figure 10 that the observed moduli for the blends B₆ (both unvulcanized and dynamically vulcanized) and B₇ (dynamically vulcanized) are close to those obtained from Kerner's rigid ma-

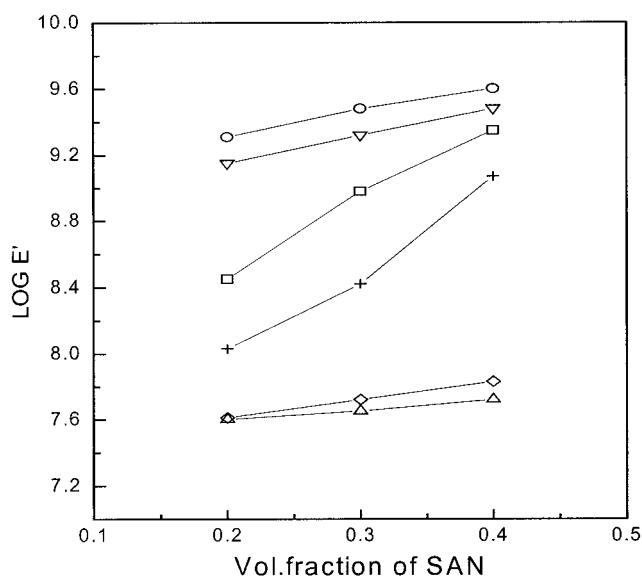


Figure 10 Storage modulus (E') versus volume fraction of SAN for different blends. Parallel model (○), series model (△), Kerner's rigid matrix-soft filler model (▽), Kerner's soft matrix-rigid filler model (◇), unvulcanized NBR/SAN blends (+), dynamically vulcanized NBR/SAN blends (□).

trix-soft filler model, suggesting the formation of SAN as the continuous matrix. For the unvulcanized blend of B₇ and for the blend B₈ (both unvulcanized and vulcanized), the experimental values are intermediate to those obtained from Kerner's rigid matrix-soft filler and soft matrix-rigid filler models. This suggests that the phases might be cocontinuous. It is also proved from the SEM photomicrographs (not shown for the blend B₈), as discussed earlier.

CONCLUSIONS

1. Thermoplastic elastomers can be prepared from the 70 : 30 NBR/SAN blend by dynamic vulcanization. The optimum concentration (in phr, based on rubber phase only) of curatives is zinc oxide, 3; stearic acid, 2; MBT, 1; TMTD, 0.5; and sulfur, 0.75.
2. The TPE composition prepared by adding a rubber-curatives masterbatch to softened SAN yields higher mechanical properties than that prepared by adding curatives to the softened plastic-rubber preblend.
3. Blends having a higher rubber-plastic ratio (60 : 40 to 80 : 20) show thermoplastic elastomeric behavior, whereas those having a higher plastic-rubber ratio (50 : 50 to 90 : 10) show the behavior of impact-resistant plastics.
4. The blends dynamically vulcanized with the sulfur-accelerator system exhibit better mechanical properties than those dynamically vulcanized with dicumyl peroxide.
5. DMTA and SEM studies reveal that the dynamically vulcanized blends (60 : 40 and 70 : 30 NBR/SAN) have SAN as the continuous phase and NBR as the dispersed phase.
6. Kerner's rigid matrix-soft filler model as applied to these blends shows good agreement with the DMTA and SEM studies.

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