

Thermoplastic Elastomeric Blend of Nitrile Rubber and Poly(styrene-co-acrylonitrile). II. Replacement of Nitrile Rubber by Its Vulcanizate Powder

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ABSTRACT: A model waste nitrile rubber powder (w-NBR) was prepared by ambient grinding of aged NBR vulcanizate based on an oil seal formulation. The w-NBR was characterized by scanning electron microscopic and optical microscopic techniques. Virgin nitrile rubber in a thermoplastic elastomeric 70:30 nitrile rubber/poly(styrene-co-acrylonitrile) (SAN) blend was replaced by w-NBR, and the mechanical properties and swelling index were determined. The virgin NBR in the blend was replaced by the rubber present in w-NBR (r-w-NBR) and the optimum mechanical properties were achieved at 45% replacement where the

blend was still reprocessable. Transmission electron microscopic and atomic force microscopic studies reveal that w-NBR particles coated with NBR are dispersed in a continuous SAN matrix. It was observed that migration of unreacted curatives from w-NBR to virgin NBR is not significant and incorporation of curatives is necessary for attainment of optimum level of mechanical properties. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 2348–2357, 2003

Key words: blends; mechanical properties; atomic force microscopy; transmission electron microscopy; swelling

INTRODUCTION

One of the various problems that humankind faces as it enters into the 21st century is how to manage and dispose waste. Since polymeric materials do not decompose easily, disposal of waste polymers is a serious environmental problem.¹

Large amounts of rubbers are used as tires for airplanes, trucks, cars, two-wheelers, etc. The disposal of tires is one of the biggest challenges. Different methods have been developed for the disposal of rubber wastes.² Recycling offers a means of disposal of polymeric wastes.³

Large-scale utilization of rubber waste could be made by incorporating ground waste rubber into plastics with a view to obtain impact-resistant plastics and thermoplastic elastomers.^{4–17} The properties of these materials depend upon the concentration of the re-grind, as well as on the adhesion between the different polymeric phases.

Naskar et al.¹⁸ observed that in thermoplastic vulcanizate formulations based on blends of ethylene-propylene–diene terpolymer (EPDM) and poly(ethyl-

ene-co-acrylic acid), 50% of the EPDM phase could be substituted by the rubber component of the ground rubber tire (GRT), and the resulting composites behave as thermoplastic elastomers. Jacob et al.¹⁹ reported partial replacement (up to 45%) of EPDM rubber in thermoplastic elastomeric EPDM/polypropylene (PP) blends by the rubber component of ground EPDM vulcanizate.

Luo and Isayev²⁰ reported development of composites based on ultrasonically devulcanized GRT and polypropylene in the ratio of 60/40 by dynamic vulcanization, using phenolic cure system and maleic anhydride grafted PP as a compatibilizer in an internal mixer and a twin-screw extruder.

Al-Malaika and Amir²¹ studied the effect of partial replacement of natural rubber (NR) by reclaimed rubber (RR) in NR/PP thermoplastic elastomer blends. It was claimed that replacement of up to half of the NR by RR is possible without significantly altering the mechanical properties of the blend. Nevatia et al.²² reported preparation and properties of thermoplastic elastomers from waste natural rubber and waste polyethylene.

Nitrile rubber (NBR), due to its excellent oil resistance, has been used in a number of applications such as oil seals, hoses, and print roller covers. A considerable amount of thermoset waste is generated as factory waste and as worn-out or failed products. Poly(styrene-co-acrylonitrile) (SAN) is a thermoplastic with high transparency, excellent gloss, high mechanical strength, and good chemical resistance.²³

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TABLE I
Details of the Materials Used

Material	Supplier/manufacturer
NBR Grade: N553NS ACN content: 34% Mooney viscosity: ML_{1+4} at 100°C, 46 M_v : 2.39×10^5 (viscometry)	Apar Industries Ltd., India
SAN Grade: Lustron sparkle ACN content: 27% M_w : 1.65×10^5 (GPC) MFI: 1.91 g/10 min at 200°C under a load of 2.16 kg.	Monsanto, USA
Zinc oxide ^a	E-Merck, Mumbai, India
Stearic acid ^a	Local supplier
IPPD ^{a,b}	ICI Ltd, Rishra, India
N770 black	Philips Carbon Black Ltd., Durgapur, India
Diocetyl phthalate	Ranbaxy Ltd., Mumbai, India
MBT ^{a,c}	ICI Ltd., Rishra, India
MBTS ^{a,d}	ICI Ltd., Rishra, India
TMTM ^{a,e}	ICI Ltd., Rishra, India
TMTD ^{a,f}	ICI Ltd., Rishra, India
Sulfur	Qualigens, Mumbai, India
1,4-dioxan, 2-butanone.	E-Merck, Mumbai, India

^aRubber grade.

^b*N, N'*-isopropyl paraphenylene diamine (antioxidant).

^cMercapto benzothiazole (accelerator).

^dMercapto benzothiazole disulfide (accelerator).

^eTetramethyl thiuram monosulfide (accelerator).

^fTetramethyl thiuram disulfide (accelerator).

Coran²⁴ reported several thermoplastic rubber-plastic blends based on NBR as the rubber phase. The plastics studied included polypropylene, polyethylene, styrene-acrylonitrile copolymer (SAN), polycarbonate, acrylonitrile-butadiene-styrene terpolymer (ABS), polystyrene, polyvinyl chloride (PVC), and nylon. He also studied a melt-mixed blend of butyl rubber and SAN.²⁴ Namboodiri et al.²⁵ reported preparation of thermoplastic elastomers from epoxidized natural rubber/SAN blend. Roy Choudhury et al.²⁶ studied the mechanical properties of the blends of NBR and polypropylene.

More recently Anandhan et al.²⁷ studied effects of dynamic vulcanization on the thermoplastic elastomeric NBR/SAN blends. It was observed that the sulfur-accelerator system leads to high mechanical properties of the dynamically crosslinked blend than the peroxide crosslinking system. While studying the effect of mixing sequence on the final properties of the blend, it was also observed that the blending of sulfur-accelerator masterbatch of the NBR with the softened SAN provides higher physical properties than when sulfur accelerator was added to the preblend of NBR and SAN.

The present article reports the results of studies on the effect of replacement of virgin rubber by a model w-NBR in a thermoplastic elastomeric composition based on nitrile rubber/poly(styrene-co-acrylonitrile).

The rubber content in the w-NBR is 60.6% by weight, which was taken into consideration while calculating total rubber content in the blend formulations.

EXPERIMENTAL

Materials

The details of the materials used are shown in Table I.

Determination of the molecular weight of nitrile rubber

The viscosity average molecular weight (M_v) was calculated by using an Ostwald viscometer.²⁸

Preparation of precursor rubber vulcanizate sheet and powder

The nitrile rubber vulcanizate powder (w-NBR) was prepared in the laboratory from a precursor vulcanizate sheet based on standard oil seal formulation: NBR (ACN content, 34%), 100; carbon black N770, 50; diocetyl phthalate, 5; zinc oxide, 5; stearic acid, 1; IPPD, 1; MBTS, 1.5; TMTM, 0.1; sulfur, 1.5; the figures are in phr (that is, parts per hundred parts of rubber, by weight). The rubber compound was prepared in a laboratory-size two-roll mill (Schwabenthan, Ger-

TABLE II
Procedure for the Preparation of Blends

Description	Mixing equipment and temperature	Mixing time and rpm
(i) NBR taken	Brabender Plasticorder at 70°C	1 min at 45 rpm
(ii) Sulfur, zinc oxide, stearic acid and w- NBR added	Brabender Plasticorder at 70°C	2 min at 60 rpm
(iii) Accelerators added	Two-roll mill at 25°C	—
(iii) Rubber compound sheeted out and cut to strips	Two-roll mill at 25°C	—
(iv) SAN softened	Brabender Plasticorder at 180°C	2 min at 30 rpm
(v) Strips of rubber masterbatch added.	Brabender Plasticorder at 180°C	4 min at 60 rpm.
(vi) Blend sheeted out.	Two-roll mill at 25°C	—

many). The optimum curing time of 6.75 min at 150°C was determined by a Monsanto Rheometer MDR-2000. An additional 10 min were provided for curing of the thick sheets of 9 mm thickness. The thick sheets were aged at 100°C in an air-aging oven for two aging periods (that is, 48 and 168 h).

The aged thick sheets were then abraded against a rotating silicon carbide wheel of a mechanical grinder (Ralliwolff TG-6 bench grinder, 2950 rpm) at room temperature. The powder was collected in a holder placed beneath the grinder.

Characterization of the vulcanizate sheet

In order to determine the mechanical properties of the aged thick sheets (9 mm), the following procedure was adopted: Thin sheets (2 mm) were molded and dumb-bell specimens were punched out from these sheets and were aged for 24, 48, 72, 96, and 120 h, respectively. The mechanical properties and the swelling parameter (a measure of the crosslink density) were determined. The swelling parameter of the aged thick sheets was also determined. The mechanical properties of the thick sheet were considered similar to that of the corresponding thin sheet of swelling parameter matched.

Vulcanizate samples were swollen in 2-butanone and the swelling parameter, which is defined as the

grams of solvent per gram of rubber hydrocarbon, was calculated as per the equation²⁹

Swelling parameter (Q)

$$= \frac{\text{Swollen weight} - \text{Dried weight}}{\text{Initial weight} \times \frac{\text{Rubber hydrocarbon weight}}{\text{Formulation weight}}} \quad (1)$$

The $1/Q$ value for the vulcanizates was taken as the apparent crosslink density.

Characterization of w-NBR powder

Density determination of w-NBR powder

The density of w-NBR powder was determined by the pycnometer method according to ASTM D 1817-96 using hexane as the noninteracting liquid at 25°C.

Morphology of w-NBR powder

The scanning electron micrographs (SEMs) of the w-NBR powder were taken in a JEOL JSM 5800 Scanning Electron Microscope (JEOL, Peabody, MA) after gold sputtering of the w-NBR powder.

TABLE III
Formulations Showing Replacement of NBR by r-w-NBR at a Constant Rubber to Plastic Ratio of 70:30 (Parts by Weight)^a

Ingredients	W ₀	W ₂₀	W ₃₀	W ₄₀	W ₄₅	W ₅₀	W ₆₀	W ₇₀
NBR	70	56	49	42	38.5	35	28	21
w-NBR ^b	0	23.1 (14)	34.7 (21)	46.2 (28)	52 (31.5)	57.8 (35)	69.3 (42)	80.9 (49)
SAN	30	30	30	30	30	30	30	30
Zinc oxide	3	3	3	3	3	3	3	3
Stearic acid	2	2	2	2	2	2	2	2
MBT	1	1	1	1	1	1	1	1
TMTD	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Sulfur	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75

^a Values in parentheses refer to the rubber content in w-NBR.

^b w-NBR was prepared by abrading thick NBR sheet aged at 100°C for 48 h.

TABLE IV
Formulations for Studying Filler Effect and Curative migration in the Rubber Phase of NBR/SAN Blend Containing r-w-NBR [values in Parentheses Refer to the Amount of Rubber Hydrocarbon in w-NBR or w-NBR (G)]

Ingredients	W_{40}	W'_{40}	WG_{40}	WG'_{40}	W''_{40}
NBR	42	42	42	42	70 ^a
w-NBR	46.2 (28)	46.2 (28)	—	—	—
w-NBR (G)	—	—	30.8 (28)	30.8 (28)	—
N770 carbon black	—	—	—	—	14 ^a
Diocetyl phthalate	—	—	—	—	1.4 ^a
Zinc oxide	2.1	—	2.1	—	2.1
Stearic acid	1.4	—	1.4	—	1.4
MBT	0.7	—	0.7	—	0.7
TMTD	0.35	—	0.35	—	0.35
Sulfur	0.53	—	0.53	—	0.53
SAN ^{b,c}	30	30	30	30	30

^a Same amount is present in w-NBR.

^b SAN was not included in for the rheometric studies (Fig. 5; Table X).

^c SAN was included in the formulations for studying the blend properties (Table XI).

Determination of particle size and size distribution using the optical microscope technique

The particles were suspended in hexane, subjected to ultrasonic dispersion, and examined under an Olympus BH-2 optical microscope (LOM) at a magnification of 200 \times . Images of representative areas were transmitted to an online Olympus Cue 2 automated image analysis system. The individual particles were identified and their respective sizes measured. The data were subsequently transferred to the EXCEL spreadsheet of a Windows-based PC and respective histograms obtained.

Preparation of the blends

The blends of NBR and SAN were prepared in a Brabender Plasticorder PLE 330 (Brabender, Ger-

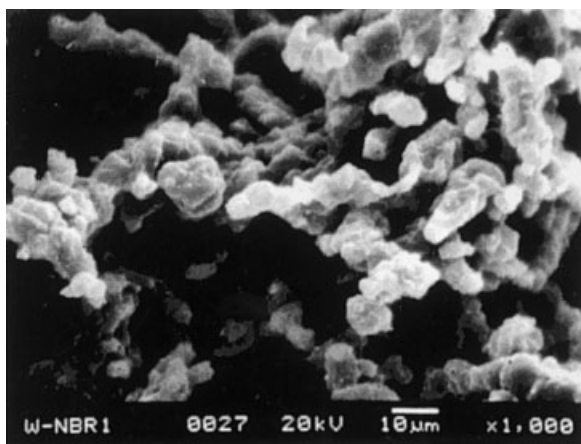


Figure 1 SEM photomicrograph of w-NBR.

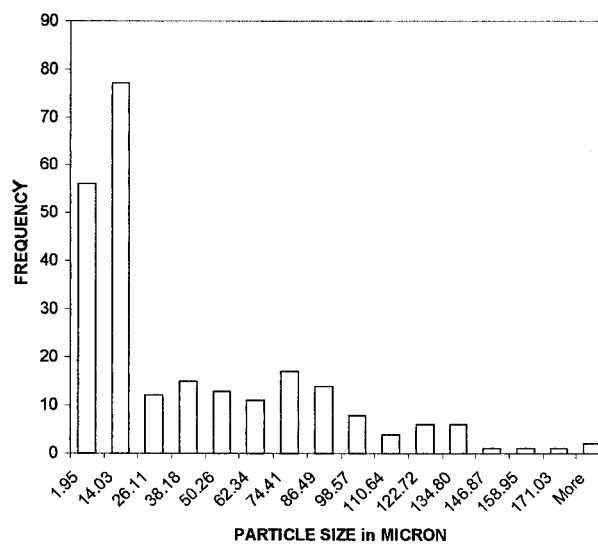


Figure 2 Particle size distribution of the w-NBR.

many) having cam-type rotors. The procedure for the preparation of the blends is given in Table II. SAN was dried at 80°C in vacuum for 3 h prior to blending. It has been shown earlier that the dynamically vulcanized 70/30 NBR/SAN blend is thermoplastic elastomeric in nature.²⁷ The 70/30 blend of NBR/SAN was dynamically vulcanized with zinc oxide, 3; stearic acid, 2; MBT, 1; TMTD, 0.5; sulfur, 0.75 (the figures are in phr). The nitrile rubber content in the blend was then gradually replaced with w-NBR, keeping the total rubber content constant. Percentage of rubber (r-w-NBR) in w-NBR is 60.6%. The blend formulations are given in Table III. Blending was done at 180°C. The blends were sheeted out in a cool two-roll mill with tight nip gap. The sheeted out blends were compression molded between aluminum sheets in a hydraulic press (Moore press, Birmingham, England) at a pressure of 5 MPa and at a temperature of 210°C and then the platens while under pressure were cooled to room temperature by water circulation.

Mechanical properties of the blends

Dumbbell specimens (ASTM die C) were punched out from the molded sheets and tensile testing was done

TABLE V
Mechanical Properties of the w-NBR Sheets (2 mm thick) Aged at 100°C for Different Periods of Time

Ageing period (hours)	Tensile strength (MPa)	Elongation at break (%)	Modulus at 100% elongation (MPa)	Swelling parameter (Q)
0	6.2	412	2.4	1.96
24	5.5	340	2.4	2.08
48	4.6	280	2.6	2.27
72	3.8	245	2.2	2.56
96	3.1	199	1.9	3.03
120	2.2	175	1.8	3.70

TABLE VI
Mechanical Properties of the NBR/SAN Blends Containing Different Amounts of r-w-NBR

Mechanical property	W ₀	W ₂₀	W ₃₀	W ₄₀	W ₄₅	W ₅₀	W ₆₀	W ₇₀
Tensile strength (MPa)	11.9	12.5	14.3	13.6	15.5	11.3	10.3	10.0
Elongation @ break (%)	267	262	235	251	224	203	141	114
Modulus @ 100% Elongation (MPa)	6.3	7.5	9.0	8.0	9.9	8.2	9.2	8.8
Tear strength (kN m ⁻¹)	60.9	62.6	50.2	63.6	73.8	60.0	58.6	54.4
Tension set @ 100% elongation (%)	24	26	20	24	24	24	26	26
Hysteresis loss (Jm ⁻² × 10 ⁻⁶)	0.111	0.134	0.167	0.151	0.185	0.158	0.173	—
Toughness (Jm ⁻²)	8464	9812	9969	9896	10292	6806	4685	3609
q in 1,4-dioxan at 35°C	3.55	3.41	3.33	3.23	3.14	3.02	2.91	2.79

at 25°C using Zwick 1445 UTM as per ASTM D 412-98a at a crosshead speed of 500 mm/min. Tear strength was determined on the angle specimens using Zwick 1445 UTM as per ASTM D 642-98. Tension set at 100% elongation was determined on the dumbbells as per ASTM D 412-98a. Hysteresis loss was determined on the dumbbells by elongating up to a strain level of 100% using Zwick 1445 UTM. Toughness of the blends was calculated from the area under the stress–strain curve.

Morphology of the blends

Transmission electron microscopy (TEM) studies

TEM studies of the representative blends were carried out by using a Hitachi H-7000 transmission electron microscope at an accelerating voltage of 75 kV and a beam current of 10 μ A.

The samples of about 50 nm thickness were prepared by cryomicrotoming of the samples in a Reichert-Jung Ultramicrotome using glass knives (made using a LKB Bromma 7800 knife maker), after freezing the specimens below their glass transition temperature (-40°C) using liquid nitrogen. The cryomicrotomed specimens were transferred to copper grids (200 mesh size) by using a tweaser. The grids were kept on glass slides and preserved in a petri dish covered with a lid.

The rubber phase (NBR) in the specimens was stained by a 2% solution of osmium tetroxide (osmium tetroxide in sodium cacodylate) for a period of 24 h.

Sample preparation for atomic force microscopy (AFM) studies

Cryomicrotoming was done in a Reichert-Jung ultramicrotome, using glass knives (made using LKB Bromma 7800 knife maker), after freezing the specimens below their glass transition temperature using liquid nitrogen. Average sample thickness was 30 μ m.

AFM measurements

AFM studies were carried out in air at ambient conditions (25°C) using a Dimension 3000 Atomic Force

Microscope, manufactured by Digital Instruments, Santa Barbara, CA, USA.

Topographic and phase (or phase contrast) images were recorded simultaneously in the tapping mode. Scanning was done using etched silicon tips (OTESPA probe), each with a nominal tip radius of curvature of 5–10 nm and spring constant in the range of 20–100 N/m. The cantilever was oscillated at its resonance frequency, which ranged between 200 and 400 kHz. The set point ratio of the cantilever that governs the tapping force was between 0.8 and 0.9 for all the scans. All the images were recorded using free oscillation amplitude of 140 ± 10 nm. The general characteristics of the probes are as follows: cantilever length, 125 μ m; cantilever configuration, single beam; reflective coating, none; sidewall angles, 17° side, 25° front, and 10° back. All the images contained 512 data points. Scan area was 30×30 μ m. For each sample, a minimum of three images were analyzed. The analysis was performed using Nanoscope III-a software version 4. The bows in the raw images were removed using the operation called flattening, which would eliminate the unwanted features from the images by calculating a

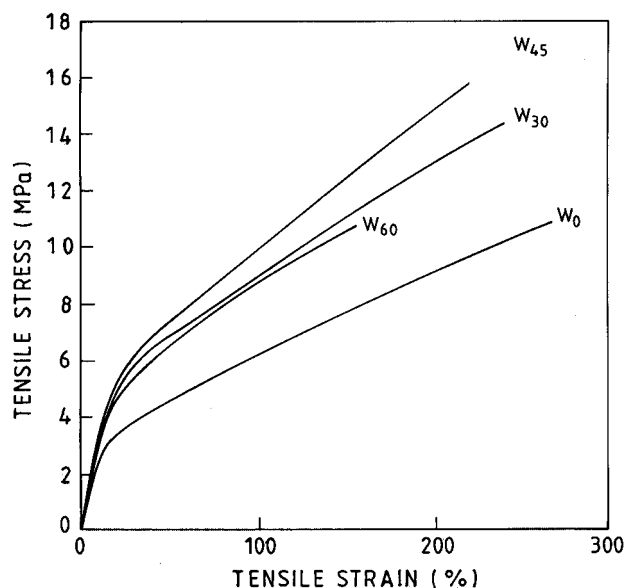


Figure 3 Tensile stress–strain curves of the representative blend samples containing different amounts of w-NBR.

TABLE VII
Effect of Aging Period of NBR Sheet Used in Preparing w-NBR on the Mechanical Properties of the Thermoplastic Elastomeric NBR/w-NBR/SAN Blend^a

Mechanical property	W ₄₅	W' ₄₅
Tensile strength (MPa)	15.5	13.4
Elongation @ break (%)	224	220
Modulus @ 100% elongation (MPa)	9.9	8.8
Tension set @ 100% elongation (%)	24	16
Tear strength (kN m ⁻¹)	73.8	61.9
Toughness (Jm ⁻²)	10292	8715
Hysteresis loss (Jm ⁻² × 10 ⁻⁶)	0.185	0.165
Swelling index (<i>q</i>)	3.14	3.81

^a Formulation same as in Table III. In W_{45'}, the aging period at 100°C of NBR sheet was 48 h; in W₄₅ the aging period was 168 h.

second-order least squares fit of the selected segment, then subtracting it from the scan line.

While doing the roughness analysis, the flattened images were subjected to a second-order plane fit in order to remove the tilt and distortions in the images. A comparison of the surface roughness can be obtained from the values of R_{ms} (that is, the root mean square average of the height deviations taken from the mean data plane), R_{max} (that is, maximum vertical distance between the highest and the lowest data points on the surface), and R_a (that is, the arithmetic average of the deviations from the center plane).

Reprocessability of the blends

In order to test thermoplasticity of the blends, the molded samples were cut in to small pieces and re-mixed in the Brabender Plasticorder at 180°C for 2 min and sheeted out and remolded. The samples were then punched out from the sheets and testing was done as per ASTM standards. The mechanical properties were determined after three cycles of mixing and molding.

Swelling studies

The swelling behavior of the blends was studied in 1,4-dioxan at 35°C. Round specimens were punched

out from the molded sheets and used for swelling studies. The swelling index (q) was calculated according to the following equation³⁰:

$$q - 1 = \{(w_2/w_1) - 1\} \cdot \rho_c / \rho_f \quad (2)$$

where w_2 is the swollen weight, w_1 the unswollen weight, q the ratio of swollen volume to original unswollen volume, ρ_c the density of the composition, and ρ_f the density of the fluid.

The swelling index (q) is used for the thermoplastic elastomers whereas the swelling parameter (Q) is used for vulcanizates.

Studies on migration of curatives and effect of filler

The formulations used in this study are given in Table IV. W₄₀ was chosen as the control formulation (Table III). W_{40'} is same as W₄₀, but without curatives. WG₄₀ is similar to W₄₀, but contains w-NBR (G) (that is, the powdered unfilled nitrile rubber) instead of filled nitrile rubber vulcanizate powder, as in W₄₀. WG_{40'} is similar to WG₄₀, but without curatives. W_{40''} contains neither w-NBR nor w-NBR (G), but it contains polymer (NBR), filler, and oil in quantities similar to that present in w-NBR. The cure parameters of the corresponding rubber compounds were determined by using a Monsanto Rheometer MDR 2000 at 180°C and 3° arc. The mechanical properties of the blends were studied by using Zwick 1445 UTM at 25°C.

RESULTS AND DISCUSSION

Characterization of w-NBR powder

The density of the w-NBR powder that was prepared from thick sheets aged for 2 days at 100°C is found to be 1.09, and the same for the one that was aged for 7 days is 1.06.

The SEM photomicrograph of the w-NBR powder is given in Figure 1. The SEM photomicrograph reveals that the vulcanizate powder has highly aggregated

TABLE VIII
Mechanical Properties of the Blends W₀ and W₄₅ After Three Cycles

Mechanical properties	W ₀			W ₄₅		
	Cycle			Cycle		
	I	II	III	I	II	III
Tensile strength (MPa)	11.9	9.7	8.8	15.5	15.8	13.7
Elongation @ break (%)	267	266	245	224	236	228
Modulus @ 100% elongation (MPa)	6.3	5.8	5.7	9.9	9.6	8.2
Tear strength (kN m ^{minus1})	60.9	59.0	58.4	73.8	70.6	67.4
Tension set @ 100% elongation (%)	24	22	20	24	20	24
Toughness (Jm ⁻²)	8464	7744	6663	10292	10941	8900
Hysteresis loss (Jm ⁻² × 10 ⁻⁶)	0.11	0.11	0.11	0.185	0.158	0.160

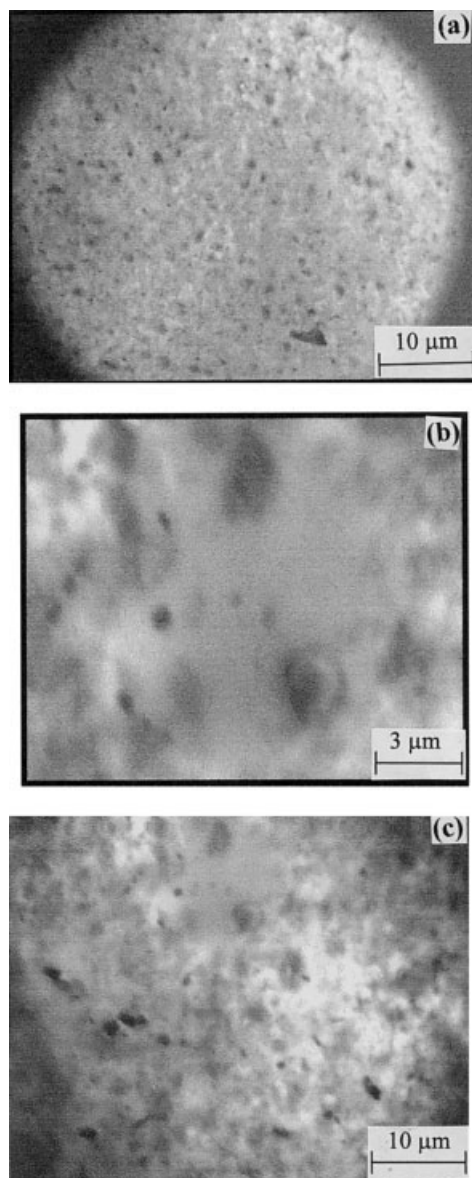


Figure 4 TEM photomicrographs showing the morphology of (a) W_0 , (b) W_{60} (showing w-NBR particles coated with virgin NBR), and (c) W_{60} (showing particles of different sizes).

chain-like structure, which breaks down during the mixing operation.

LOM studies reveal that the particle size ranges from 1 to 135 μm and the average particle size is 36 μm . The particle size distribution is shown in Figure 2. However, particles larger than 135 μm and smaller than 1 μm are very small in number (particles in the range of 1–3 μm are seen in TEM photomicrographs).

The mechanical properties of the 2 mm thick sheets (aged for different time periods) used in the preparation of w-NBR along with the swelling parameter (Q) values are given in Table V. The swelling parameter of the 9 mm thick sheets aged for 48 h is 2.14. It matches that ($Q = 2.08$) of the 2 mm thick sheet aged for 24 h.

So, its mechanical properties can be considered to be similar to that of the 2 mm thick sheet aged for 24 hours. The swelling parameter of the 9 mm thick sheet aged for 144 h is 3.24. This is closer to that ($Q = 3.03$) of the 2 mm thick sheet aged for 96 h. So, its mechanical properties can be considered to be similar to that of the 2 mm thick sheet aged for 96 h.

Mechanical properties of the thermoplastic elastomeric blends containing w-NBR

The mechanical properties of the 70/30 NBR/SAN dynamically vulcanized thermoplastic elastomeric blends containing different amounts of w-NBR are given in Table VI and the tensile stress–strain curves of the representative samples are given in Figure 3. The tensile strength and modulus at 100% elongation increase up to 45% replacement of NBR by w-NBR in the blend, after which the values fall drastically. The elongation at break decreases gradually up to 45% replacement and then abruptly beyond that level of replacement. Toughness increases gradually up to 45% replacement of NBR by w-NBR in the blend. Beyond 45%, toughness decreases abruptly. Hysteresis loss, however, increases gradually with replacement level and remains almost constant beyond 30% replacement of NBR by w-NBR in the blend. Tear strength reaches a maximum at 45% replacement, beyond which it decreases. The mechanical properties are optimum at 45% replacement of the NBR phase (in the NBR/SAN blend) by r-w-NBR, when tensile strength of the composition is 15.5 MPa, elongation at break is 224%, modulus at 100% elongation is 9.9 MPa and tension set at 100% elongation is 24%. The properties of the w-NBR/NBR/SAN blend conform to those of thermoplastic elastomeric composition.³¹ The properties drop and the processing becomes difficult when the replacement level of NBR by r-w-NBR is beyond 45%. The properties of the blend containing w-NBR prepared from 9 mm thick sheets aged for 168 h are given in Table VII. It is evident that the mechanical properties drop down to some extent if the precursor w-NBR vulcanizate (thick sheet) is aged for a longer time before grinding. This may be due to the higher extent of degradation of the sheets aged for longer time. This is evident from the swelling index (q) values (Table VII).

Reprocessability of the blends

The mechanical properties of representative blends (that is, W_0 and W_{45}) after three cycles of remixing and remolding are shown in Table VIII. The changes in properties are within acceptable limits, indicating satisfactory reprocessability of the blends, behaving as thermoplastic elastomers.

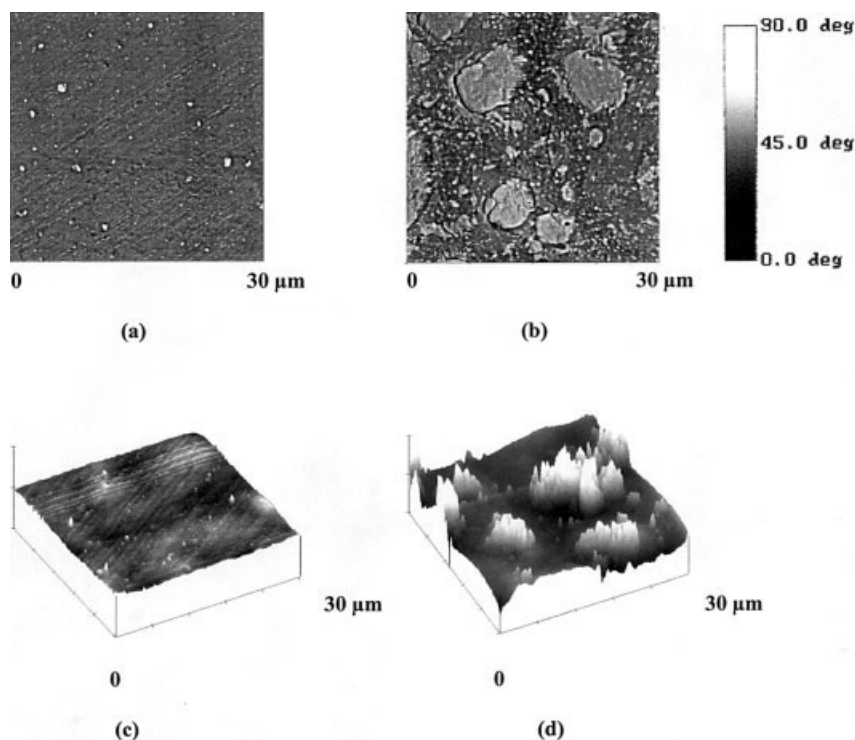


Figure 5 AFM images showing the morphology of (a) W_0 and (b) W_{60} (phase contrast images); (c) W_0 and (d) W_{60} (3D images).

Morphology of the blends

TEM studies

The TEM photomicrographs of the representative samples of the blends W_0 and W_{60} are shown in Figure 4(a) and (b). It can be seen that the blends have two-phase morphology. The dark phase corresponds to the NBR phase, which has been stained by osmium tetroxide, and the lighter phase corresponds to the SAN phase. In the case of the blend W_0 (control), the average size of the dispersed particles is in the range of 0.8–1 μm . From Figure 4(b), it is apparent that SAN forms the continuous phase, while virgin NBR tends to form the dispersed phase encapsulating the dispersed w-NBR particles. The light-colored virgin NBR coating on the dark w-NBR particles is also seen in Figure 4(b). Naskar et al. observed similar morphology in the case of GRT particles coated with EPDM in a high density polyethylene matrix.¹⁸ Figure 4(c) is the TEM photomicrograph of the blend W_{60} in which the dispersed particles in the size range of 1–3 μm are seen.

AFM studies

The AFM phase contrast images of the representative samples of the blends W_0 and W_{60} are given in Figure 5(a) and 5(b) and the corresponding three-dimensional (3D) images are given in figure 5(c) and 5(d) respectively. As observed in the case of TEM photomicro-

graphs, it is evident that the nitrile rubber vulcanizate powder is dispersed in the SAN matrix. The darker portion in the phase contrast images corresponds to the hard SAN phase, and the brighter portion corresponds to the softer NBR phase. In the case of the 3D images, hills and valleys are seen. The hills correspond to the NBR phase and the valleys correspond to the SAN phase. Dispersed NBR particles in the size range of 1–7 μm are seen in the phase image of W_{60} [Fig. 5(b)].

The roughness values of the blends are given in Table IX. Generally, if a surface is flat and contains no large deviations from the mean surface level, R_{ms} and R_a will be similar. However, if a surface is very rough and there are appreciable numbers of large bumps and holes, R_{ms} will be larger than R_a .³² For all these blends, R_{ms} values are larger than the R_a values. So, it is evident that the surface of these blends is very rough and there must be bumps and holes of appreciable amount.

TABLE IX
Roughness Values of the TPE Containing w-NBR

Blend designation	R_{ms} (nm)	R_{max} (nm)	R_a (nm)	Surface area (μm^2)
W_0	77.6	727.4	63.0	138.4
W_{30}	85.1	1085.0	65.9	149.7
W_{45}	103.5	1111.0	80.5	152.2
W_{60}	100.4	1096.8	80.2	153.9

TABLE X
Dispersion Factor of the Blends

Blend designation	R_{ms} (nm)		$D_f = R_{ms}(\text{image})/R_{ms}(\text{box})$
	Image	Box	
W_0	77.6	73.6	1.05
W_{30}	85.1	79.0	1.08
W_{45}	103.5	94.0	1.10
W_{60}	100.4	105.8	0.95

The roughness values can be correlated with the mechanical properties of the blends. The tensile strength and modulus at 100% elongation increase with increasing roughness values. The R_{ms} roughness values of these blends are in the following order: $W_0 < W_{30} < W_{45} > W_{60}$. From Table V, we can see that the hysteresis loss values of these blends also follow the same order. This is due to increased molecular friction due to increased roughness. The same trend had been observed earlier for carbon black filled EPDM rubber.³³

The extent of dispersion of the w-NBR powder in these thermoplastic elastomeric compositions can be evaluated by the dispersion factor (D_f), defined as the ratio of R_{ms} (image) to the R_{ms} (box) value. If the D_f value is very close to unity, the dispersion can be considered to be uniform. The D_f values of these blends are given in Table X. It can be seen that the D_f values are near unity for all these blends and hence it can be concluded that the dispersion of w-NBR is uniform in all the cases.

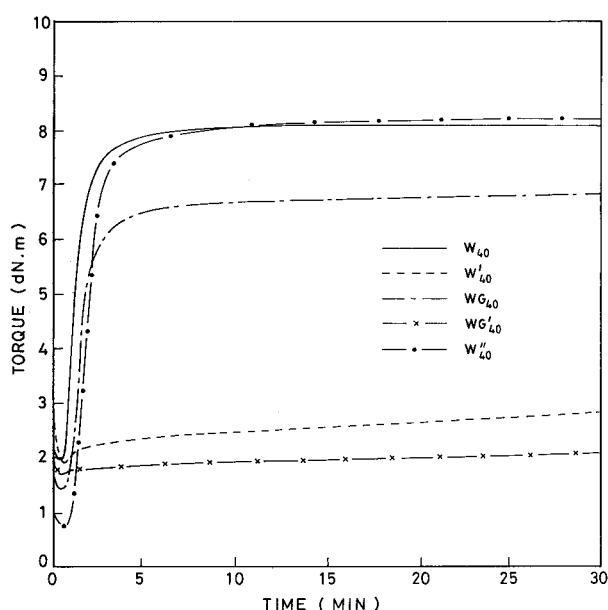


Figure 6 Monsanto rheographs of the rubber compounds (Table IV) used in the study of migration of additives and effect of filler on blend properties.

TABLE XI
MDR Results of the Rubber Compounds Used in the Study of Migration of Additives and Filler Effect (Formulations as in Table IV)

MDR data	W_{40}	W'_{40}	WG_{40}	WG'_{40}	W''_{40}
M_L (dN m)	1.87	1.96	1.40	1.68	0.74
M_H (dN m)	8.10	2.78	6.84	2.12	8.20
$M_H M_L$ (dN m) (Δ torque)	6.23	0.82	5.44	0.44	7.46

Swelling behavior

The swelling behavior of the thermoplastic elastomeric blends containing different amounts of w-NBR was studied in 1,4-dioxan at 25°C. The values of swelling index (q) are summarized in Table VI. The swelling index gradually decreases on incorporation of w-NBR. This may be due to the presence of increasing amount of filler that is present in w-NBR. It thus leads to increased polymer–filler interaction and thereby restricts the extent of swelling.

Effect of curatives and filler present in w-NBR on the properties of NBR/w-NBR/SAN blends

Rheographs obtained for the corresponding rubber compounds of the formulations (Table IV) used in this study (i.e., formulations without SAN) are shown in Figure 6 and the curing parameters are summarized in Table XI. The mechanical properties of the compositions are given in Table XII. The following observations can be made:

1. Δ torque in the Monsanto rheographs in the case of W_{40}' and WG_{40}' is not significant, indicating that migration of curatives from w-NBR to virgin NBR is not significant. Consequently, the physical properties of the corresponding blends are also poor.³⁴

TABLE XII
Mechanical Properties of the NBR/SAN Blends Used in the Study of Migration of Additives and Filler Effect (Formulations as in Table IV)

Mechanical property	W_{40}	W_{40}'	WG_{40}	WG'_{40}	W''_{40}
Tensile strength (MPa)	13.6	5.7	12.4	4.4	14.8
Elongation @ break (%)	251	66	262	77	276
Modulus @ 100% elongation (MPa)	8.0	^a	10.7	^a	11.9
Tension set @ 100% elongation (%)	24	^a	24	^a	10
Tear strength (kN m^{-1})	63.6	49.0	72.8	38.6	65.6
Toughness (Jm^{-2})	9896	1948	9675	1827	11389
q in 1,4-dioxan at 35°C	3.23	6.21	4.54	7.32	2.89

^a Could not be determined.

2. Comparison of the properties of W_{40} with W_{40}' and WG_{40} with WG_{40}' show that incorporation of curatives is necessary for attainment of proper degree of crosslinking.
3. Comparison of WG_{40} with W_{40}'' reveals that filler (N770 carbon black) reinforces the thermoplastic elastomeric composition.
4. Comparison of W_{40} with W_{40}'' shows that filler reinforcement effect is less in W_{40} , because part of the filler in w-NBR might be covered by the rubber phase, which is not available for reinforcing the virgin NBR phase in the NBR/SAN blend. This can be seen from the TEM photomicrograph also [Fig. 4 (b)].

Thus, it can be concluded that the filler present in w-NBR contributes significantly to the mechanical properties of the blends, whereas the migration of curatives from w-NBR to virgin NBR plays an insignificant role. Kuriakose et al.³⁵ reported that reinforcing fillers cause enhancement in mechanical properties of thermoplastic elastomeric rubber/plastic blends and the effect is more pronounced in the case of blends with high rubber content.

CONCLUSIONS

1. The ambient ground model waste nitrile rubber powder has a highly aggregated chain-like structure as revealed by the SEM photomicrograph.
2. The model waste nitrile rubber powder could be used in place of virgin NBR in a dynamically vulcanized thermoplastic elastomeric 70:30 blend of NBR/SAN. Up to 45% of the virgin NBR could be replaced by the rubber content (r-w-NBR) of the model waste NBR powder without appreciable loss in mechanical properties. The blend containing 45% of r-w-NBR was found to be reproducible.
3. Both the TEM and AFM studies reveal that NBR is dispersed in a continuous SAN matrix. Furthermore, TEM studies reveal that virgin NBR forms a coating on the w-NBR particles.
4. AFM results show good dispersion of w-NBR in the matrix. Roughness values of the blends obtained from the AFM studies correlate well with the mechanical properties.
5. From the MDR studies, it is evident that migration of unreacted curatives from w-NBR to virgin NBR is not significant, and incorporation of curatives is necessary for attainment of proper degree of crosslinking and optimum level of mechanical properties. However, filler present in w-NBR contributes to some extent to the reinforcement of the thermoplastic elastomeric blend.

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