

Self-Vulcanizable Rubber Blend Based on Neoprene and Carboxylated Nitrile Rubber: Effect of Blend Ratio on Miscibility and Physical Properties

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SYNOPSIS

Mill mixed blend of neoprene and carboxylated nitrile rubber can be vulcanized during molding at high temperatures (180°C) in the absence of any vulcanizing agent, which is supported by FTIR studies. The extent of vulcanization reaction depends not only upon the molding time but also on the blend ratio. Dynamic mechanical analyses and differential scanning calorimeter studies show that neoprene and carboxylated nitrile rubber are not miscible at the segmental level in the self-vulcanized blend.

INTRODUCTION

It has been observed by De and co-workers¹⁻⁷ that mill mixed blends of rubbers having appropriate functional groups can be made to interact with each other and thus vulcanized at high temperatures in the absence of any curatives. Examples include blends based on epoxidized natural rubber (ENR)-chlorosulfonated polyethylene (Hypalon),^{1,6} ENR-carboxylated nitrile rubber (XNBR),^{2,4} Hypalon-XNBR,⁵ and polyvinyl chloride (PVC)-XNBR.⁷ It has also been reported³ that a 1 : 1 blend of neoprene and carboxylated nitrile rubber gets vulcanized during molding at 190°C in the absence of any vulcanizing agent. Further studies on this reveal that the extent of vulcanization reaction depends not only on time and temperature of vulcanization, but also on the proportion of each constituent present in the blend. In the present communication, we report the results of our studies on the effect of blend ratio on miscibility and physical properties.

EXPERIMENTAL

Neoprene AC was procured from DuPont Ltd., USA. XNBR used was Krynac-221 containing high level

of carboxylated monomer and medium high bound acrylonitrile level and was procured from Polysar Ltd., Canada. The formulation of the mixes are given in Table I. The mixes are denoted by N₁₀₀, N₇₅, N₅₀, and N₂₅, the subscripts corresponding to the weight percentage of neoprene in the blends. N₀ corresponds to 100 wt % of XNBR.

Both neoprene and XNBR were masticated separately on 14 × 6 in. two-roll mixing mill to the similar Mooney viscosity. Then they were blended on the mill for about 6 min. Mooney viscosity and Mooney scorch time were determined at 120°C as per ASTM D 1646-1963 by using a Negretti automation Mooney shearing disc viscometer, Model MK-III. Rheographs of the blends were taken at 180°C on a Monsanto rheometer R-100. The blends were molded at 180°C for 60 min.

In order to compare the self-vulcanization system with that of the conventional methods of vulcanization, neoprene and XNBR were vulcanized by conventional methods with vulcanizing agents. Formulations of these single rubbers are given in Table I. For comparison purposes we chose the N₇₅ blend, and, in order to nullify the effect of crosslink density on properties, the single systems were vulcanized at 150°C to the same crosslink density as that of the N₇₅ blend by molding to the time when the rise of the rheometric torque (i.e., the difference between maximum torque and minimum torque) is the same in N₇₅, N₁₀₀, and N₀. These times are 60 min for N₇₅, 8 min for N₁₀₀, and 36 min for N₀.

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Table I Formulations of the Mixes

	N ₁₀₀	N ₇₅	N ₅₀	N ₂₅	N ₀
Neoprene	100	75	50	25	—
XNBR	—	25	50	75	100
Zinc oxide	5	—	—	—	3
Magnesium oxide	4	—	—	—	—
Stearic acid	—	—	—	—	1.5
Sulfur	—	—	—	—	0.3
MOR ^a	—	—	—	—	1
Na 22 ^b	0.5	—	—	—	—

^a *N*-oxydiethylene benzothiazole-2-sulfenamide.

^b Ethylene thiourea.

The following physical properties of the vulcanizates were determined according to the standard methods: Tensile strength (Zwick UTM, ASTM D 412-87), tear resistance (Zwick UTM, ASTM D 624-86, using an unnicked 90° angle specimen, die C), hardness (Shore A, ASTM D 2240-86), resilience (Dunlop tripsometer, BS:903:Part A8:1963—method A), compression set (ASTM D 395-85—method B, where the specimens were subjected to compressive deformation for 22 hours at 70°C), heat buildup (Goodrich flexometer, ASTM D 623-78, with a load of 24 lb and stroke of 4.45 mm), and abrasion resistance (Dupont abrasion tester, BS:903:Part A9:1957—method C).

Infrared spectra of neoprene, XNBR, and their 75/25 blend were obtained in the thin film form by using a Perkin Elmer 1600 FTIR spectrometer. An average of 16 scans at 4 cm⁻¹ resolution was used. The films of neoprene and XNBR were prepared by molding at 100°C for 2 min, whereas the blend was molded at 180°C for 60 min.

Dynamic mechanical properties were measured using a Toyo-Baldwin Rheovibron Model DDV-III-EP at a strain amplitude of 0.0025 cm and frequency of 3.5 Hz. The procedure was to cool the sample to -100°C and record the measurements during warmup. The temperature rise was 1°C/min.

Differential scanning calorimeter (DSC) measurements were done on a DuPont differential scan-

ning calorimeter, Model 910 in nitrogen atmosphere. Glass transition temperatures (T_g 's) of the samples were taken as the midpoint of the step in the scan, run at a heating rate of 20°C/min.

The volume fraction of rubber, V_r , in solvent swollen blend was calculated from equilibrium swelling data by the method reported by Ellis and Welding⁸:

$$V_r = [(D - FT)/\rho_r] / [(D - FT)/\rho_r + A_0/\rho_s]$$

where T is the weight of the specimen, D its deswollen weight, F the weight fraction of insoluble components, A_0 the weight of absorbed solvent corrected for swelling increment, and ρ_r and ρ_s are the densities of rubber and solvent, respectively. Chloroform was used as the solvent for present study.

RESULTS AND DISCUSSION

Processing behavior of the blends as measured by Mooney viscometer is shown in Table II. It has been found that incorporation of neoprene in the blends increases the Mooney viscosity but reduces scorch time. The very long scorch time of the blends show excellent processing safety in comparison to single rubber mixes (N₁₀₀ and N₀).

Rheographs of different mixes are shown in Fig-

Table II Processing Characteristics of the Blends of Neoprene and XNBR

Mix No.	N ₁₀₀	N ₇₅	N ₅₀	N ₂₅	N ₀
Mooney viscosity					
ML ₍₁₊₄₎ at 120°C	20	32	30	28	32
Mooney scorch time at					
120°C (min)	9	55	78	153	4

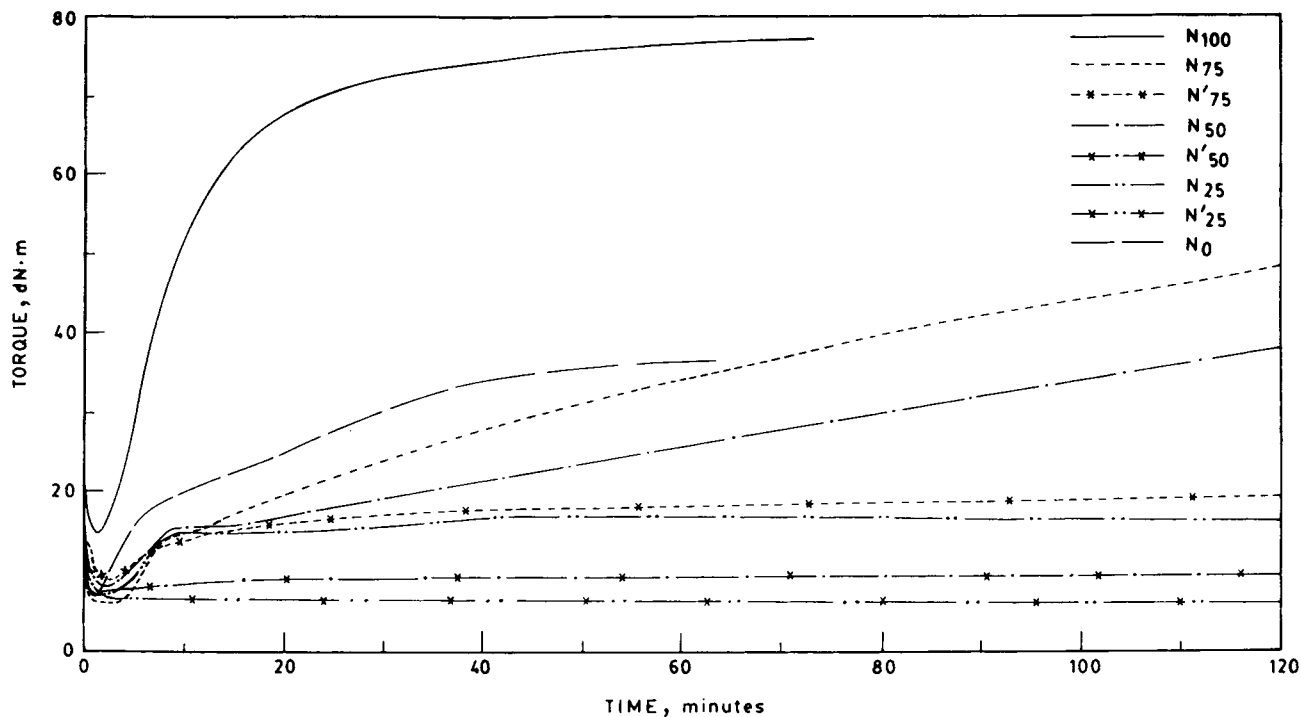


Figure 1 Rheographs of neoprene/XNBR (N_{75} , N_{50} , and N_{25}) and neoprene/natural rubber (N'_{75} , N'_{50} , and N'_{25}) blends at 180°C. N_{100} (neoprene) and N_0 (XNBR) represent the rheographs of the single rubbers at 150°C.

ure 1. Although the single rubbers (neoprene and XNBR) show broad plateau in the rheographs, in case of blends we observed a gradual increase in rheometric torque with vulcanization time. This indicates progressive crosslinking between the blend constituent themselves. The marching increase in modulus implies that cure reversion is absent in practice and the vulcanizate network is thermally stable at 180°C. It is also evident from the rheographs that the extent of crosslinking reaction depends on the blend composition and it is maximum for 75/25 blend of neoprene/XNBR. Mechanical properties and V_r , volume fraction of rubber in swollen vulcanizate, discussed later in this paper, also substantiate this finding. However, neoprene is reported to undergo thermovulcanization at elevated temperature.⁹ It is not known whether thermovulcanization of neoprene will take place in the presence of rubbers having active functional groups like XNBR. In order to eliminate the effect of thermovulcanization, we have taken rheographs of blends of neoprene and natural rubber, which does not contain any active functional groups, in the same blend composition as that of neoprene and XNBR. In Figure 1, blends N'_{75} , N'_{50} , and N'_{25} correspond to neoprene/natural rubber composition of 75/25, 50/50,

and 25/75, respectively. It is believed that, in the same blend composition, rheometric torque in the neoprene/natural rubber system corresponds to thermovulcanization alone whereas, in the case of the neoprene/XNBR system, the torque rise corresponds to thermovulcanization of neoprene as well as self-vulcanization between neoprene and XNBR. At a particular curing time the difference in the two torque values will correspond to the torque due to self-vulcanization only. The calculated rheographs thus obtained are shown in Figure 2. Here the torque rise recorded with temperature is expected to be solely due to crosslinking between neoprene and XNBR. However, this thermovulcanization is prominent only in the blend where neoprene content is high, e.g., 75/25 blend of neoprene/XNBR and it is insignificant in the case of the other two blends (Fig. 1).

Fourier-transform infrared (FTIR) spectroscopy is a useful tool for studying the nature and intensity of interactions in polymer blends.¹⁰ In its most simple form, this approach consists of following any shifts on mixing of band positions for units, or occurrence of a new band, indicating the formation of a new linkage caused by the interaction of the reactive groups present in the two polymers. The ev-

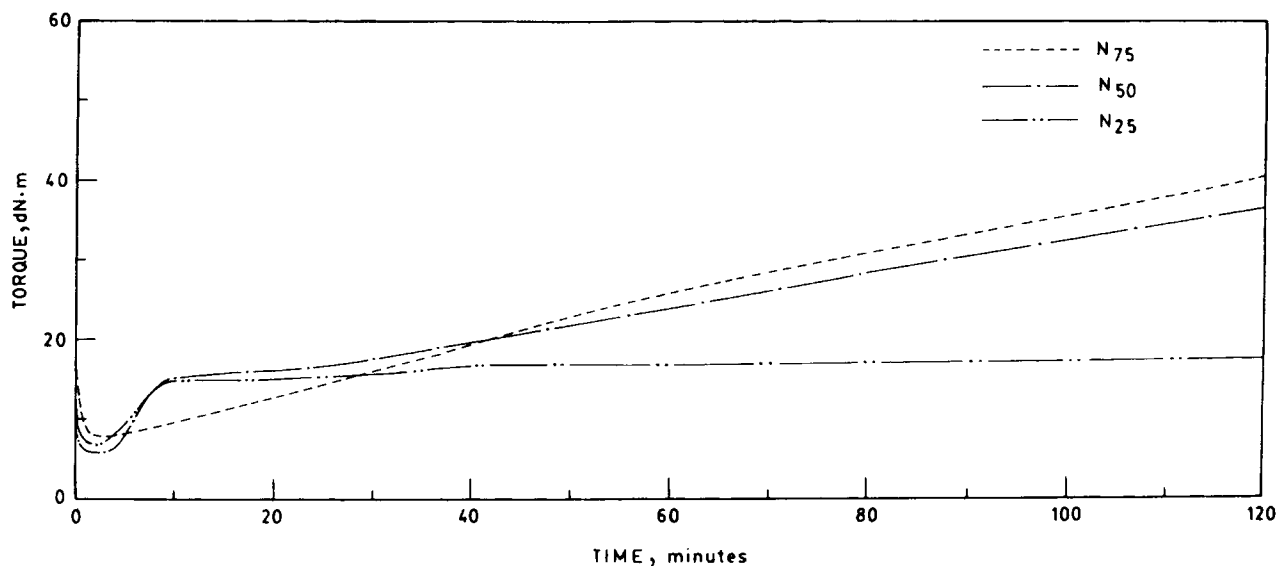


Figure 2 Calculated rheographs of the self-vulcanizable neoprene/XNBR blends after deducting the effect due to thermovulcanization of neoprene.

idence for interaction between neoprene and XNBR in the present system suggests examining (i) the possibility of shifts of bands associated with polar groups C=O and C=N in XNBR and C-Cl in neoprene and (ii) formation of ester linkage.

Figure 3 shows the FTIR spectra for neoprene (a), XNBR (b), their 75/25 blend (c), and their difference spectrum (d). The characteristic peaks of neoprene for C-Cl stretching vibration occurs at 660, 607, 571, and 535 cm^{-1} and C=O stretching vibration of carboxylic acid in XNBR occurs at 1696 cm^{-1} . As can be seen from Figure 3(c), the intensity of the band associated with symmetric C=O stretching mode (1696 cm^{-1}) for carboxylic acid in XNBR and C-Cl stretching vibration for CH_2Cl in neoprene is greatly reduced in the blend. Moreover, a new peak is observed in the blend at 1767 cm^{-1} , which is due to the C=O stretching vibration of lactone, which is also detected when a difference spectrum [Fig. 3(d)] is computed. The crosslinking between allylic chlorine of neoprene and carboxyl group of XNBR can occur by two mechanisms, either by ester formation (mechanism I) or by lactone formation (mechanism II), as shown in Figure 4. Occurrence of the 1767 cm^{-1} band in the IR difference spectra (Fig. 3) shows the latter as the probable mechanism.

Although both neoprene and XNBR are soluble in chloroform, the molded blend is insoluble in the same solvent, showing that each blend constituent gets crosslinked by the other during molding. The weight loss after 48 h of immersion in chloroform

is less than 8%, which indicates high degree of crosslinking. This is also evident from V_r (volume fraction of rubber in the swollen vulcanisate), shown in Table III.

The difference in deformation characteristics of the blends under uniaxial tensile stress is shown in Figure 5. The XNBR-rich blend (N_{25}) exhibits viscoelastic deformation of a very soft rubber and breaks at high strain. However, a higher proportion of neoprene in the blends increases the modulus and tensile strength. The 75/25 blend of neoprene/XNBR registers minimum elongation but the highest tensile strength. This is due to the maximum extent of crosslinking as evident from the rheographs (Fig. 2) and V_r values (Table III). Physical properties of the blends are summarized in Table III. Higher proportion of neoprene in the blends, in general, results in improved physical properties. As the proportion of neoprene in the blend increases, modulus, tear strength, hardness, and resilience increase, but elongation at break, heat buildup, and compression set decrease. Although hysteresis properties are better in neoprene-rich blends, abrasion loss is found to be more in these blends as compared to XNBR-rich blends, since XNBR (N_0) has a higher abrasion resistance as compared to neoprene (N_{100}) (Table III). A comparison between single rubbers (N_{100} and N_0) and the corresponding blend (N_{75}) indicates that, with respect to some properties, the blend registers intermediate values like tensile and tear strength, whereas, with respect to modulus, abrasion resistance, set, resilience, heat

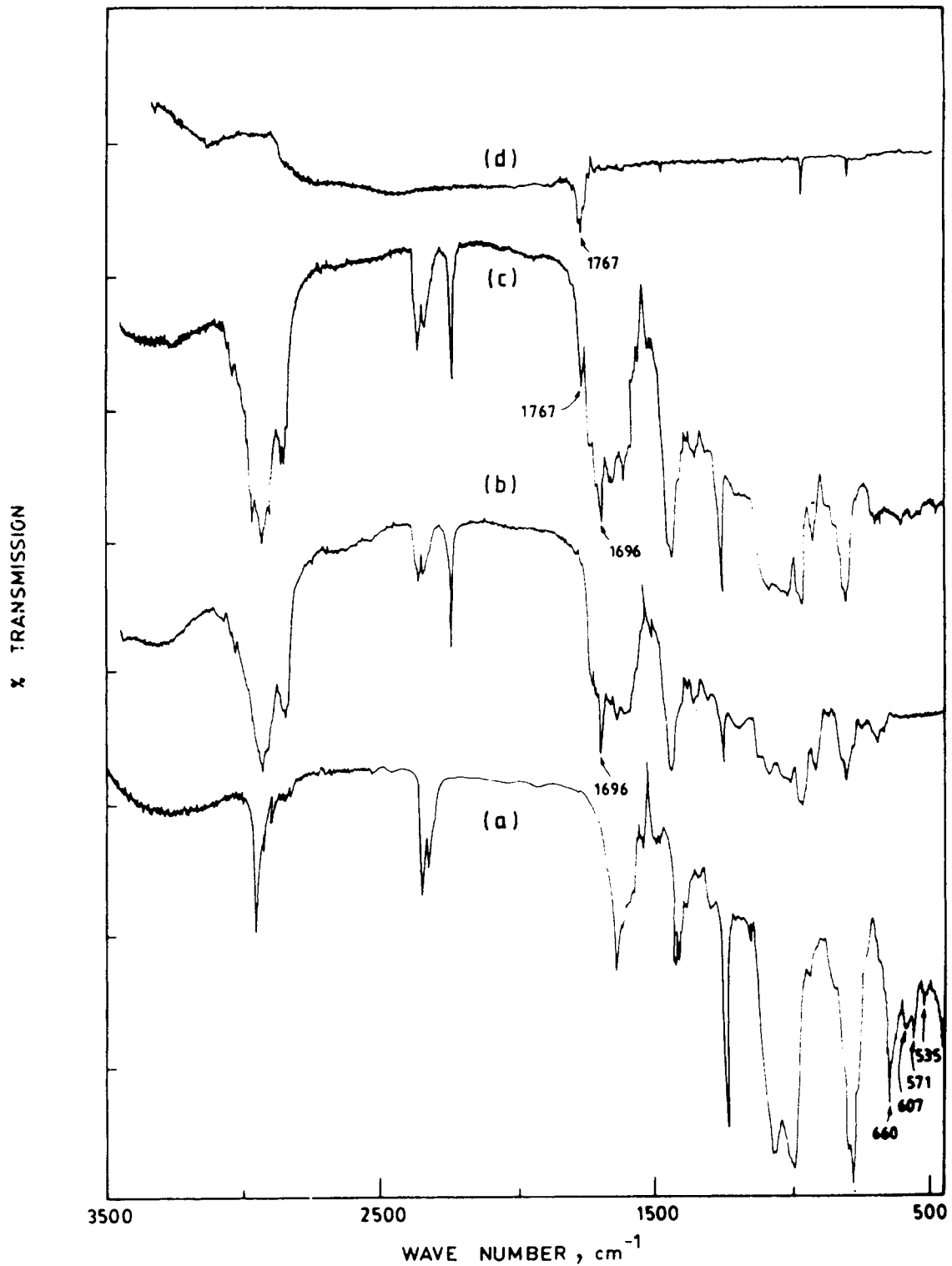


Figure 3 FTIR spectra of neoprene (a), XNBR (b), N₇₅ (c), and their different spectrum (d).

buildup, and hardness, the blend is closer to single neoprene vulcanizate. But, with respect to elongation at break, it is closer to single XNBR vulcanizate.

It has been indicated earlier that both the single rubbers and the blend N₇₅ were of similar crosslink density and the properties accordingly are not due

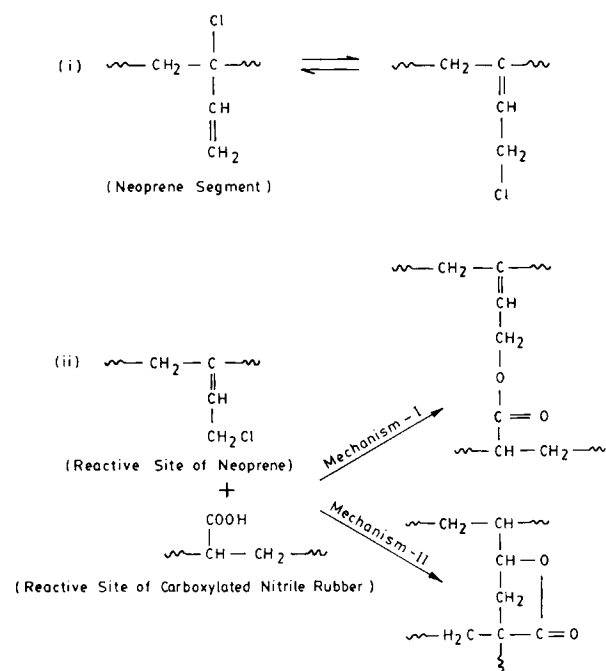


Figure 4 Proposed mechanism of reaction between neoprene and XNBR.

to difference in extent of crosslinking but due to type of crosslinking.

In order to understand the abrasion mechanism, we have analyzed SEM fractographs of the abraded surfaces of neoprene, XNBR, and their blends. Neoprene shows characteristic flow of material in

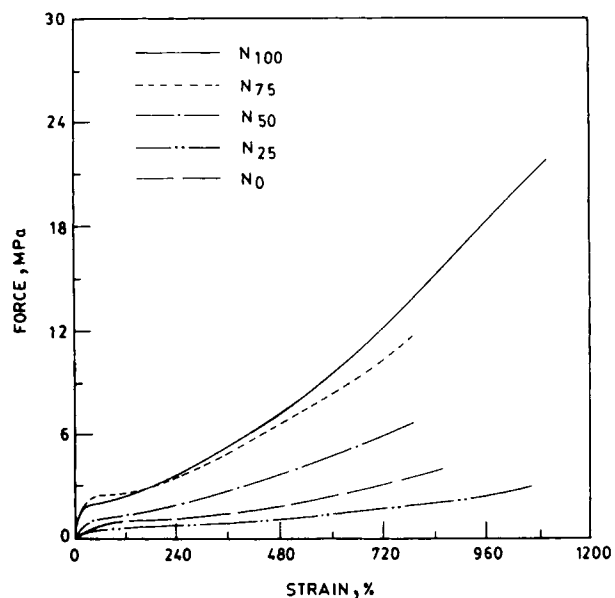


Figure 5 Stress-strain behavior of neoprene, XNBR, and their blends.

the direction of application of frictional force experienced by the specimen surface when sliding against the abrasive wheel (Fig. 6). It shows low abrasion resistance (Table III). Studies on failure of neoprene vulcanizate by Setua and De¹¹ also support this observation.

XNBR shows excellent abrasion resistance (Table III). The failure surface of XNBR after an abra-

Table III Effect of Blend Ratio on Physical Properties of Neoprene/XNBR Blends

Mix No.	N ₁₀₀	N ₇₅	N ₅₀	N ₂₅	N ₀
100% modulus (MPa)	2.25	2.52	1.56	0.61	0.89
300% modulus (MPa)	4.34	4.17	2.30	0.79	1.26
Tensile strength (MPa)	22.39	11.17	6.77	2.70	3.69
Elongation at break (%)	1102	781	842	998	798
Tear strength (N/mm)	52.00	30.00	21.00	12.00	15.00
Abrasion loss (cc/h)	2.8	2.7	1.9	1.5	0.3
Compression set at					
(a) Constant stress (%)	9	6	9	24	38
(b) Constant strain (%)	24	22	31	42	65
Goodrich Flexometer test					
(a) Heat buildup <i>T</i> (°C)	18	28	56	57 ^a	b
(b) Dynamic set (%)	2	3	10	—	b
Resilience (%)	58	52	49	46	62
Hardness, Shore A	81	73	65	43	43
<i>V_r</i> , volume fraction of rubber in swollen vulcanizate	0.19	0.18	0.11	0.09	0.18

^a Sample had blown out after 5 min.

^b Sample is very soft; it is not possible to perform the test.

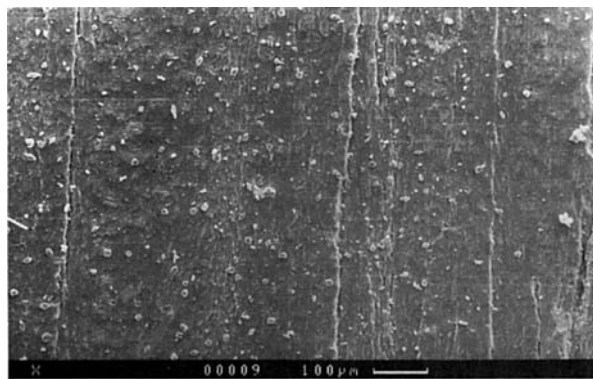


Figure 6 SEM fractograph of the abraded surface of neoprene.

sion period of 10 min shows ridges parallel to the direction of abrasion showing abrasive type of wear (Fig. 7). Low ridge height and close spacing of the ridges indicates high abrasion resistance.¹²

Blending with neoprene lowers the abrasion resistance of XNBR. Figures 8–10 show the abraded surfaces of the blends of neoprene and XNBR. The 25/75 blend of neoprene/XNBR shows ridge formation perpendicular to the direction of abrasion indicating high abrasion resistance which is close to XNBR vulcanizate. It follows frictional type of wear. In case of 50/50 blend, ridges are less prominent and the material starts flowing in the direction of abrasion. It gives abrasion resistance value in between that of neoprene and XNBR. However, the flow of material is more pronounced in case of the 75/25 blend of neoprene/XNBR, showing poor abrasion resistance like the neoprene vulcanizate.

In order to examine the miscibility of neoprene/XNBR blend, the clarity of the films, obtained by compression molding at 180°C, was first checked. The films were found to be opaque, indicating that

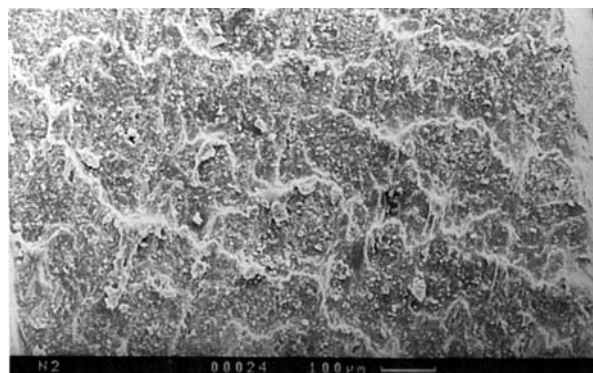


Figure 7 SEM fractograph of the abraded surface of XNBR.

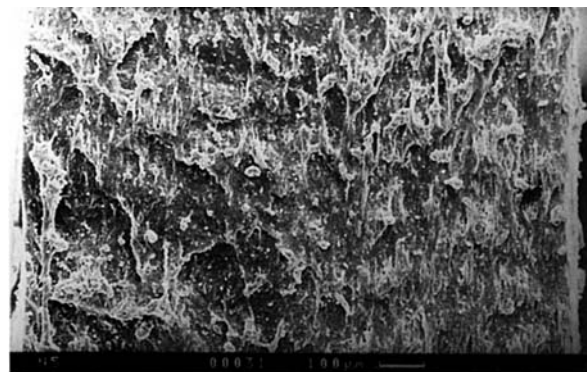


Figure 8 SEM fractograph of the abraded surface of 25/75 blend of neoprene/XNBR.

the polymer pairs are not miscible at the segmental level. However, the final evidence in support of immiscibility is available from determination of glass transition temperature. Dynamic storage modulus (E'), loss modulus (E''), and damping ($\tan \delta$) of different compositions of neoprene/XNBR blend are shown in Figures 11–13.

Dynamic storage modulus rapidly decreases at the T_g zone due to the decrease in stiffness of the samples. Concomitantly, loss modulus and damping sharply rise till they attain the maxima and then fall down with increase in temperature. Temperature corresponding to the maxima in damping or loss modulus is chosen as the T_g of the samples. As a general trend in the polymer system, the temperature corresponding to the loss modulus maximum, in all cases, is found to be lower than that of damping maximum.

Pure neoprene is observed to show two transitions in the rubbery region as reflected from plots of damping and elastic modulus. For neoprene there is a sharp transition in elastic modulus around -25°C

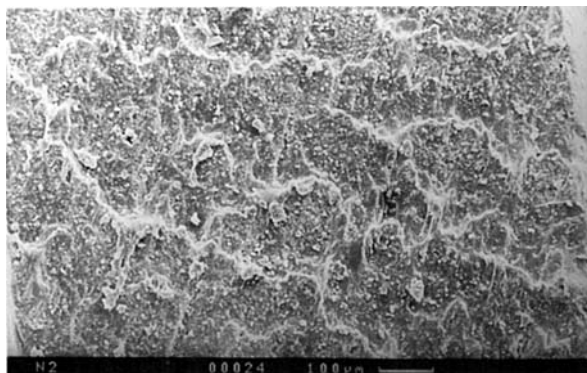


Figure 9 SEM fractograph of the abraded surface of 50/50 blend of neoprene/XNBR.

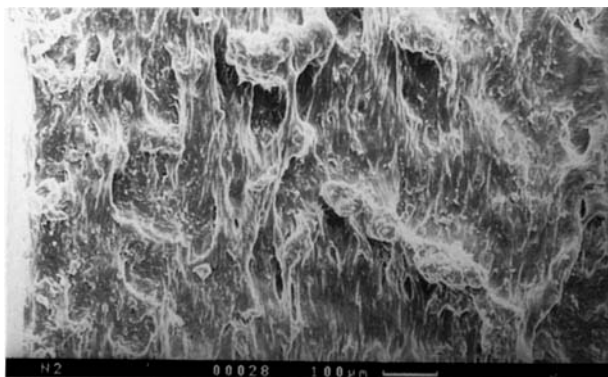


Figure 10 SEM fractograph of the abraded surface of 75/25 blend of neoprene/XNBR.

and a slow second transition around -13 – $+36^{\circ}\text{C}$. In the plots of damping versus temperature, the maximum damping occurs at -29.4°C . In neoprene

the first sharp transition observed in damping and elastic modulus is due to transition from glassy to rubbery region, and the second transition is due to the melting of the crystallites since the polymer contains about 90% *trans*-1,4-polychloroprene.¹³ Development of crystallinity at low temperatures for elastomers have been reported earlier.^{14,15} Pure XNBR shows a single transition in the T_g region.

Two glass transitions for the blends indicate the presence of two phases in the blends. The higher T_g should correspond to a phase composed principally of XNBR and the lower T_g corresponds to a phase wherein neoprene is the major composition, and this is an indication that each polymer dissolves the other to an extent that depends on overall blend composition.¹⁶ Again shifting of the T_g 's away from the T_g 's of the single components indicates very strong interaction between the two phases.¹⁷ Figure 11 shows the $\tan \delta$ spectra over the entire range of ex-

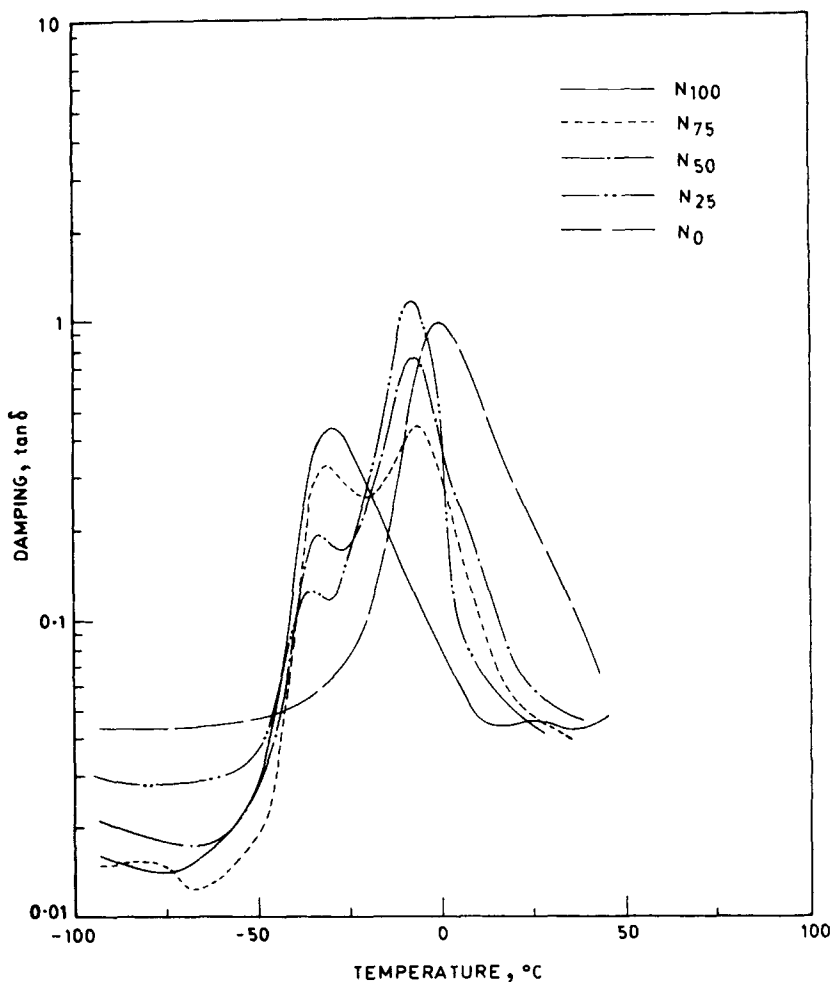


Figure 11 Mechanical damping of neoprene, XNBR, and their blends at different temperatures.

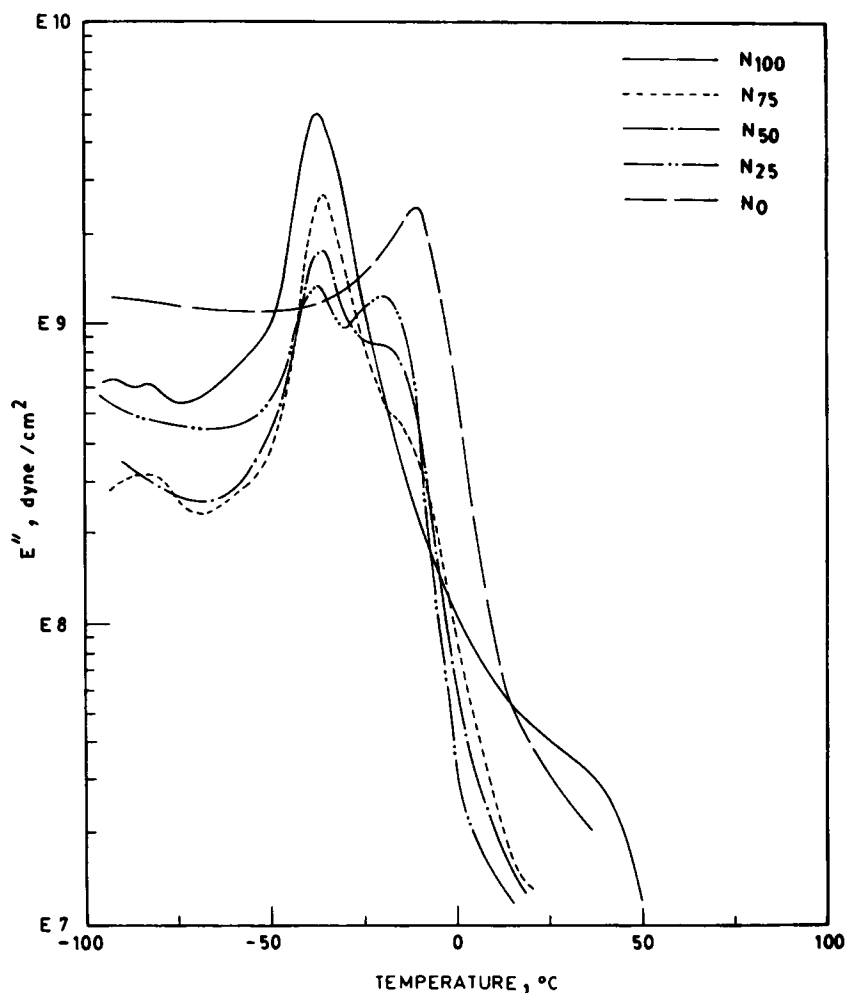


Figure 12 Storage modulus (E') of neoprene, XNBR, and their blends at different temperatures.

perimental temperature (-100 – $+50^{\circ}\text{C}$) for neoprene/XNBR blends. It is apparent from the figure that $\tan \delta$ peak height for XNBR decreases and that for neoprene increases as the neoprene content in

the blend increases. It was also observed that addition of neoprene in the blends broadens the transition peaks as well as brings them close to each other. It has been reported¹⁸ that with increase in

Table IV Glass Transition Temperature (T_g 's) of Neoprene/XNBR Blends as Obtained from Dynamic Mechanical Analysis (DMA)

	Damping Maximum $\tan \delta$	Loss Modulus Maximum E''	Width of the Transition Zone in Storage Modulus versus Temperature Plot, ΔT ($^{\circ}\text{C}$)
N_{100}	-29.4	-37.2	77
N_{75}	-31.3, -7.1	-30.2, -15.2	58
N_{50}	-33.2, -7.2	-35.2, -21.1	54
N_{25}	-35.2, -7.7	-37.1, -21.1	39
N_0	0	-9.0	23

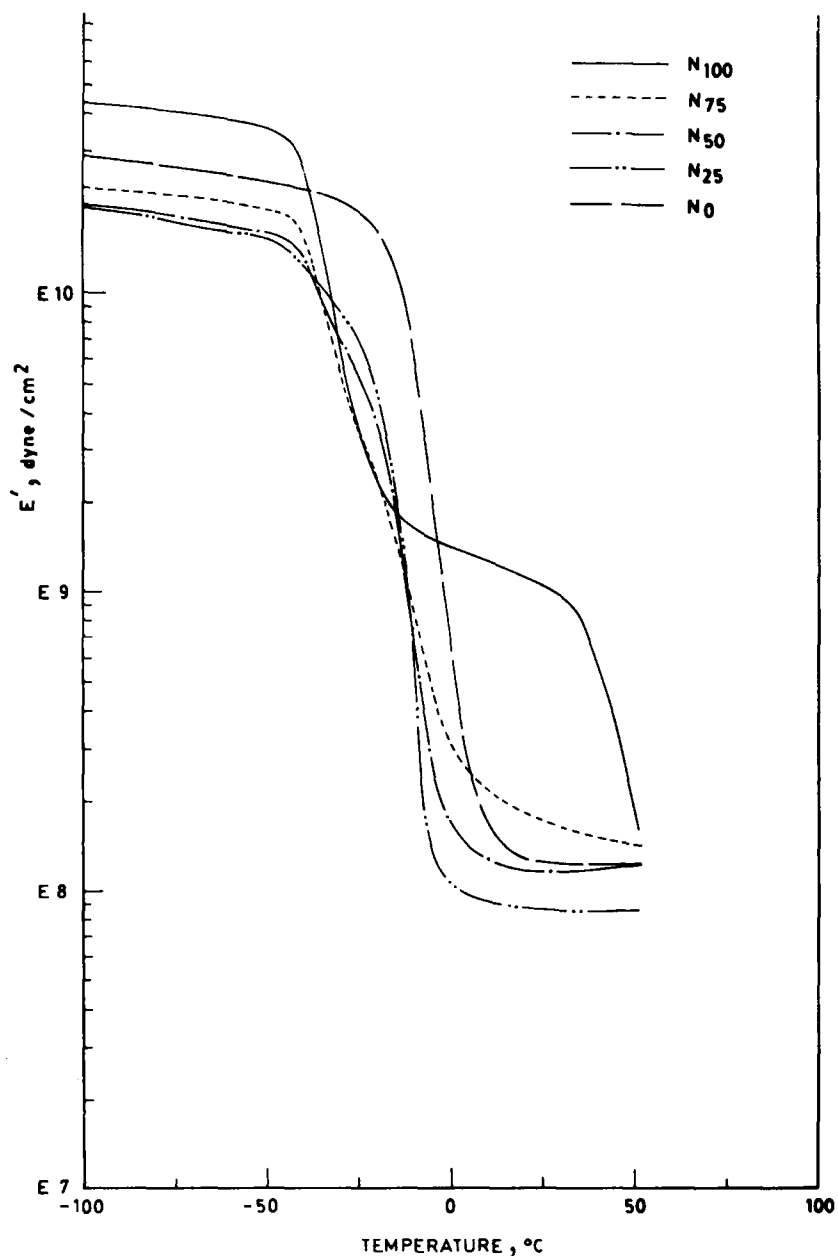


Figure 13 Loss modulus (E'') of neoprene, XNBR and their blends at different temperatures.

extent of crosslinking, the maximum of the dynamic damping peak reduces and the width of the peak broadens.

The rheometric torque values (Fig. 2) and V_r , the volume fraction of rubber in swollen vulcanizates (Table III), also substantiate the fact that, with increase in neoprene content in the blend, the extent of crosslinking reaction increases. Dynamic mechanical properties substantiate these findings. The dynamic damping is a sensitive characterization of

extent of crosslinking in polymers.¹⁸ The glass transition temperatures as obtained from dynamic mechanical analyses and the width of the transition zone in storage modulus are summarized in Table IV.

CONCLUSIONS

1. Mill mixed blend of neoprene and carboxylated nitrile rubber gets vulcanized during

molding at high temperatures (say, 180°C) in the absence of any vulcanizing agent.

2. Crosslinking of one rubber constituent by the other in the blend has been confirmed by Monsanto rheometry, solvent swelling, and FT-IR studies.
3. Mooney viscometry studies show that such self-vulcanizable rubber blends exhibit excellent processing safety.
4. Physical properties of such blend vulcanizates depend on blend composition and are similar to conventional rubber vulcanizates.

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