

A Self-Vulcanizable and Miscible Blend System Based on Hypalon and Carboxylated Nitrile Rubber

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SYNOPSIS

Blends of hypalon and carboxylated nitrile rubber can be vulcanized during molding at high temperatures without addition of any curing agent. This is supported by studies on a Monsanto rheometer, solvent swelling, and FTIR spectroscopy. We designate such a blend system as "self-vulcanizable rubber blend." Dynamic mechanical analyses and differential scanning calorimeter studies show that hypalon and carboxylated nitrile rubber form a completely miscible blend. Physical properties of the blends are comparable to that of control single-rubber vulcanizates. The blend can be reinforced by carbon black filler.

INTRODUCTION

It is known that hypalon can be cross-linked by polyfunctional alcohols.^{1,2} Accordingly, we thought that it should also be possible to cross-link hypalon by the functional group of a terpolymer-like carboxylated nitrile rubber (abbreviated XNBR). While studying the blend of hypalon and XNBR, we observed that the blend gets vulcanized during molding. Since no curative was used, we designate such a system as "self-vulcanizable rubber blend." Studies on Fourier transform infrared spectroscopy (FTIR) support the proposed mechanism of reaction between hypalon and XNBR. In the present communication, we report the results of our preliminary studies on self-vulcanizable hypalon/XNBR blend. Earlier, De et al. reported similar self-vulcanizable rubber-blend systems based on epoxidized natural rubber/hypalon,^{3,4} neoprene/XNBR,^{5,6} and XNBR/epoxidized natural rubber.^{7,8}

EXPERIMENTAL

The XNBR used was Krynac-221 containing a high level of carboxylated monomer and medium-high-

bound acrylonitrile level and was procured from Polysar Ltd., Canada. Hypalon-40 was procured from DuPont Ltd., U.S.A. Both hypalon and XNBR were masticated separately on a 14 in. × 6 in. two-roll mixing mill for about 2 min. Then, they were blended on the mill for about 4 min. Cold water was circulated through the rolls to keep the temperature low in order to avoid sticking of rubbers on the rolls. The mill temperature for the initial mastication step was 29°C. The temperature rise during the mixing of gum compound was only 4°C. For filled compound, filler was added gradually after blending the two rubbers and then mixed thoroughly for an additional 4 min. The temperature rise in case of filled blends was 6°C. Total mixing time was about 8 min for unfilled and 12 min for filled systems. Table I shows the blend compositions and the formulations of the mixes involving single rubbers, i.e., hypalon and XNBR. Mixing of compounding ingredients with single rubbers was completed within 9 min for gum and 14 min for filled mixes.

Mooney viscosity and Mooney scorch time were determined at 120°C as per ASTM D1646-1963 by using a Negretti Automation Mooney shearing disc viscometer, Model MK-III. Rheographs of the blends (both gum and filled) were taken at 170°C on a Monsanto rheometer, R-100. The blends were cured at 170°C for 60 min. The control mixes were vulcanized at 150°C to the same extent of cross-linking as that of the 50/50 blend of hypalon/

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Table I Formulations of the Mixes

	X ₁₀₀	X ₅₀	X ₀	X _{100C}	X _{50C}	X _{0C}
Krynac-221	100	50	—	100	50	—
Hypalon-40	—	50	100	—	50	100
ISAF carbon black	—	—	—	20	20	20
Zinc oxide	3	—	—	3	—	—
Magnesium oxide	—	—	10	—	—	10
Stearic acid	1.5	—	—	1.5	—	—
Sulfur	0.3	—	—	0.3	—	—
MOR ^a	1	—	—	1	—	—
Tetrone A ^b	—	—	1.5	—	—	1.5

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

^b Dipentamethylene-thiuram tetrasulphide.

XNBR by keeping the rise in rheometer torque the same. The corresponding cure times for the blends and single-rubber mixes are shown in Table II.

The following physical properties of the vulcanizates were determined according to the standard methods. Tensile strength (Zwick UTM, ASTM D412-87), tear resistance (Zwick UTM, ASTM D624-86, using an unnicked 90° angle specimen, die C), hardness (shore A, ASTM D2240-86), resilience (Dunlop tripsometer, BS: 903: Part A8: 1963—method A), compression set (ASTM D395-85—method B, where the specimens were subjected to compressive deformation for 22 h at 70°C), and abrasion resistance (DuPont abrasion tester, BS: 903: Part A9: 1957—method C).

The hysteresis behavior of the blend vulcanizates was determined from the ratio of the retraction energy to the ratio of input energy of deformation up to the point of strain reversal, recorded by the electronic integrator attached to the Instron Universal Testing Machine, Model 1195. The samples were pulled to the desired extension (200%) and retracted at a crosshead speed of 100 mm/min.

The volume fraction of rubber, V_r , in the solvent swollen blend was calculated from equilibrium swelling data by the method reported by Ellis and Welding⁹:

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

where T is the weight of the specimen, D is its de-swollen weight, F is the weight fraction of insoluble components, A_0 is 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 the present study.

Infrared spectra of hypalon, XNBR, and their 1 : 1 blend were taken in film form by using Perkin-Elmer 1600 FTIR spectrometer. An average of 16 scans at 4 cm⁻¹ resolution was used. The films of hypalon 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 warm-up. The temperature rise was 1°C/min.

Differential scanning calorimeter (DSC) measurements were done on a DuPont differential scanning calorimeter, Model 910, in nitrogen atmosphere. Glass transition temperatures of the samples were taken as the midpoint of the step in the scan, run at a heating rate of 20°C/min.

RESULTS AND DISCUSSION

Processing behavior of the blends and the single components as measured by a Mooney viscometer is shown in Table II. Mooney viscosity of the gum blend is in between the values of the two single rubbers. Incorporation of reinforcing ISAF carbon black filler increases the Mooney viscosity in all cases, as expected. However, the increase is less marked in the case of single XNBR and extreme in the case of blend.

The Mooney scorch time of blend is close to hypalon alone. Incorporation of reinforcing ISAF carbon black reduces the scorch time in all cases. However, the reduction is extreme in the case of blend and less marked in the case of single rubbers.

Table II Processing Characteristics of Hypalon, XNBR, and Their Blends

	X ₁₀₀	X ₅₀	X ₀	X _{100C}	X _{50C}	X _{0C}
Mooney viscosity ML ₍₁₊₄₎ at 120°C	32	24	12	40	38	20
Mooney scorch time at 120°C (min)	4	46	44	3	18	40
Cure time (min)	23	60	6	28	60	9

Rheographs of the different mixes are shown in Figure 1. The marching increase in rheometer torque with vulcanization time indicates progressive cross-linking between hypalon and XNBR. It also implies that the cure reversion is absent and the vulcanizate network is thermally stable at the test temperature (170°C). To understand that the increase in rheometric torque is solely due to the self-vulcanization between hypalon and XNBR and not for slow ther-

mal curing of the individual rubbers, rheographs of neat hypalon and XNBR were taken at 170°C. As is seen from Figure 1, there is no rise in rheometer torque for the pure components, which indicates the absence of any thermal cure of the single components at 170°C. Studies on solvent swelling and FTIR, as discussed later, also substantiate the fact that each blend constituent gets vulcanized by the other during molding at high temperature.

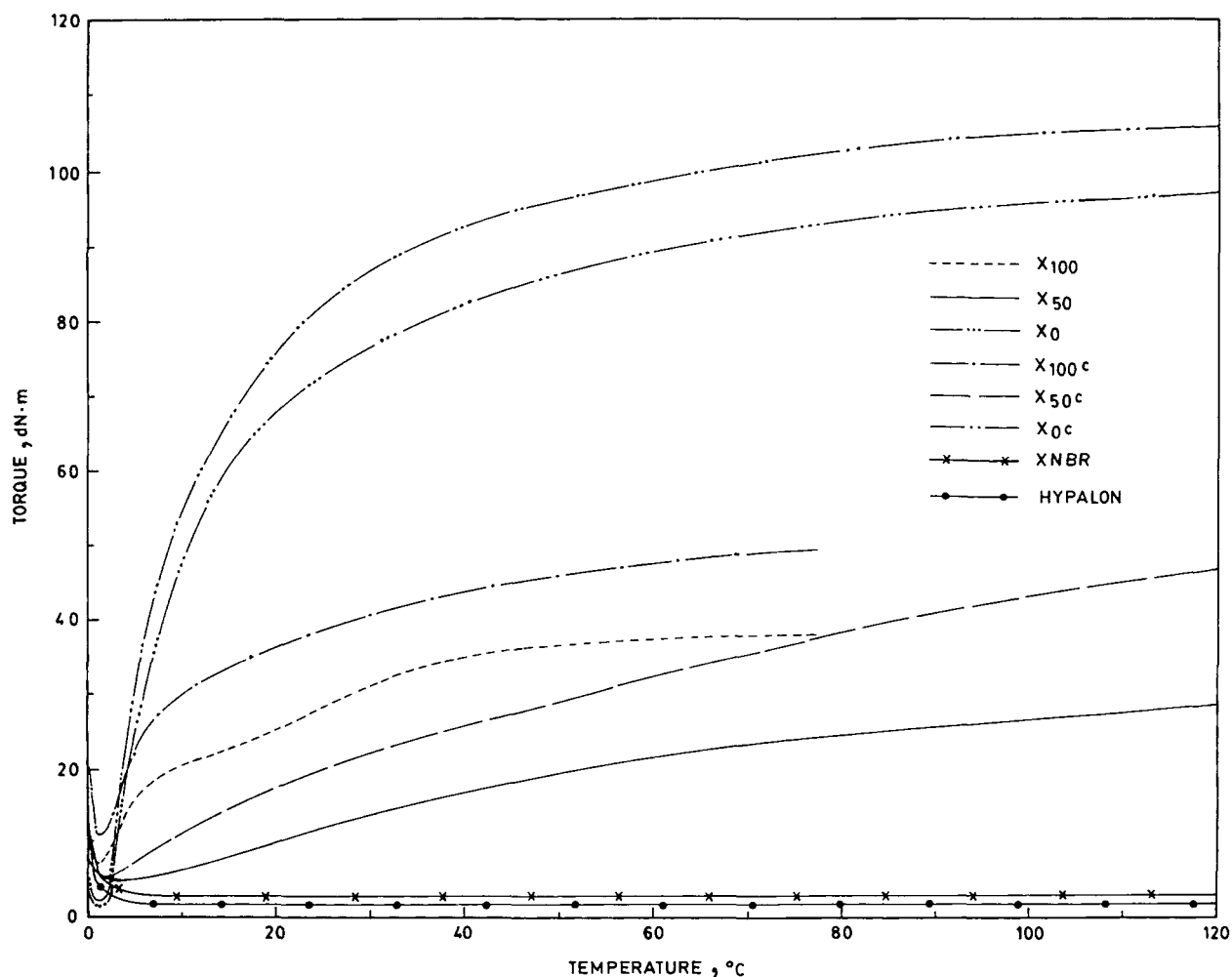


Figure 1 Rheographs of hypalon/XNBR blends (X₅₀ and X_{50C}) at 170°C. X₁₀₀, X_{100C} and X₀, X_{0C} represent the rheographs of the single-rubber mixes (Table I) at 150°C. Hypalon and XNBR represents the rheographs of neat hypalon and XNBR at 170°C.

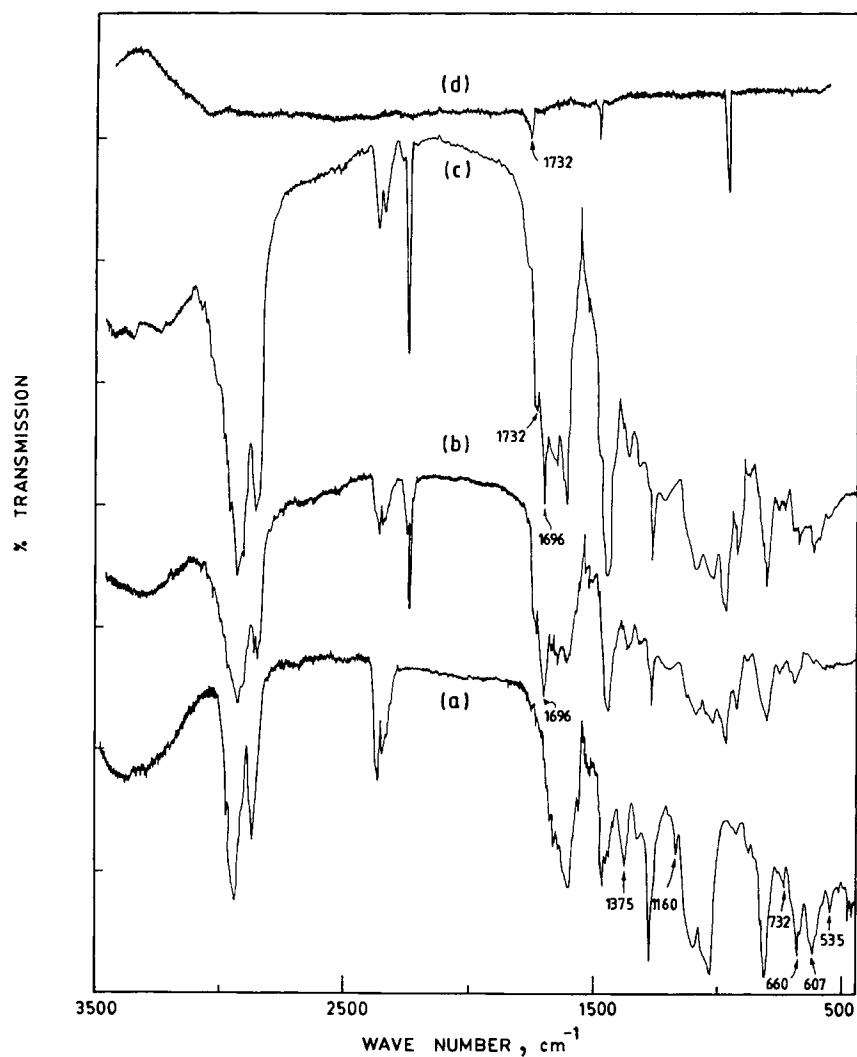


Figure 2 FTIR spectra of hypalon (a), XNBR (b), the 50/50 blend (c), and their difference spectrum.

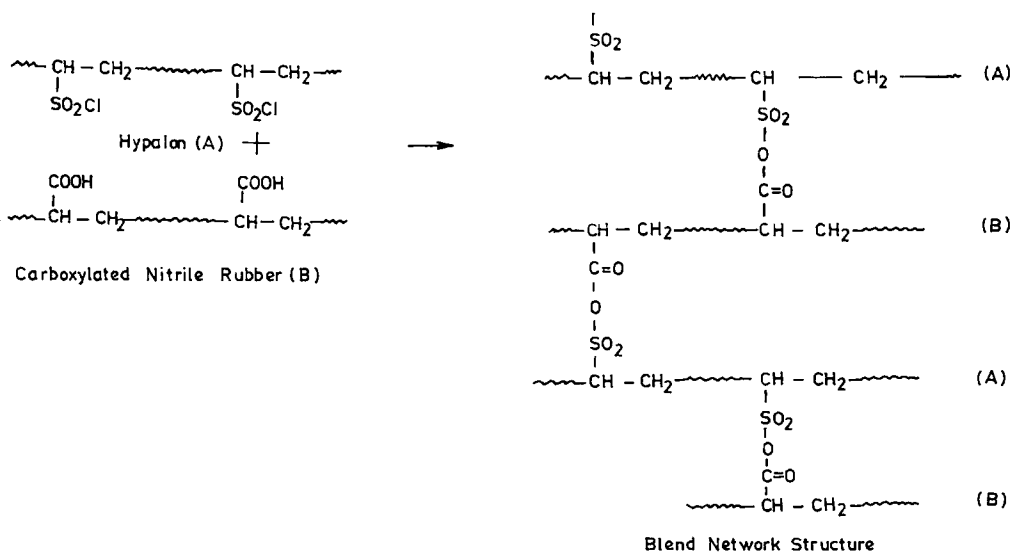


Figure 3 Proposed mechanism of reaction between hypalon and XNBR.

Table III Physical Properties of Hypalon, XNBR, and Their 50/50 Blend

	X ₁₀₀	X ₅₀	X ₀	X ₁₀₀ C	X ₅₀ C	X ₀ C
Modulus, 100% (MPa)	0.72	0.60	1.23	1.70	1.39	2.30
Modulus, 300% (MPa)	0.91	0.62	3.10	3.97	3.33	8.46
Tensile strength (MPa)	3.09	2.32	11.31	14.12	10.02	17.40
Elongation at break (%)	798	1500	676	739	884	573
Tear strength (N/mm)	11.45	10.15	20.80	24.12	40.15	37.00
Abrasion loss (cc/h)	0.5	1.6	0.2	0.3	0.5	0.2
Compression set at						
Constant stress (%)	39	14	34	35	13	26
Constant strain (%)	67	29	62	65	28	54
Resilience (%)	56	49	45	51	43	43
Hardness, Shore A	43	40	52	52	50	65
V _r , volume fraction of rubber in swollen vulcanizate	0.10	0.09	0.09	0.19	0.18	0.17

Addition of 20 phr of ISAF carbon black increased the rheometric torque of the blend, as in X₅₀C, indicating strong polymer–filler interaction. This phenomenon is very similar to that of conventional rubber systems. The control single rubber mixes show a broad plateau in the rheographs (Fig. 1).

Although both hypalon and XNBR are soluble in chloroform, the molded blend is insoluble in the same solvent, showing that each blend constituent gets cross-linked by the other during molding. The weight loss after 48 h of immersion in chloroform is less than 13%, which indicates a high degree of cross-linking.

Figure 2 shows the FTIR spectra of hypalon (a), XNBR (b), and the 50/50 blend (c) and their difference spectrum (d). The characteristic peaks of hypalon for SO₂ asymmetric and symmetric stretching vibration occur at 1375 and 1160 cm⁻¹, respectively, and that for the C–Cl stretching vibration at 660, 607, and 535 cm⁻¹. The peak for the C=O stretching vibration of carboxylic acid in XNBR occurs at 1696 cm⁻¹. It can be seen from

Figure 2(c) that the intensity of the bands associated with the symmetric C=O stretching mode (1696 cm⁻¹) in XNBR and with the SO₂ asymmetric and symmetric stretching vibration (1375 and 1160 cm⁻¹) in hypalon are greatly reduced. Moreover, a new band at 1732 cm⁻¹ is observed in the blend that

Table IV Hysteresis Behavior of Different Blends

Blend	Cycle No.	Hysteresis Loss (%)	Set (Arbitrary Units—Instron Chart)
X ₅₀	1	46	6
	2	32	3
	3	30	2
X ₅₀ C	1	54	5
	2	36	3
	3	34	2.5

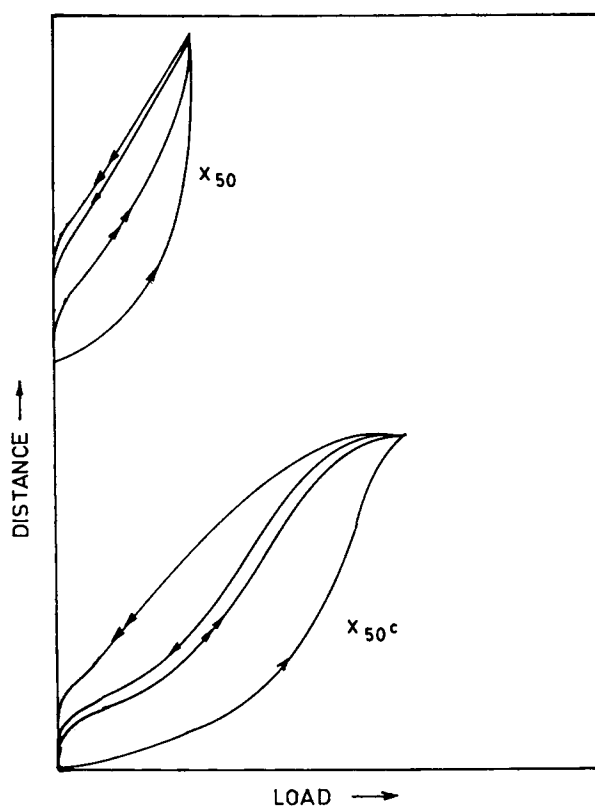


Figure 4 Hysteresis curves for blend X₅₀ and X₅₀C at 200% extension. Both chart speed and crosshead speed are 100 mm/min.

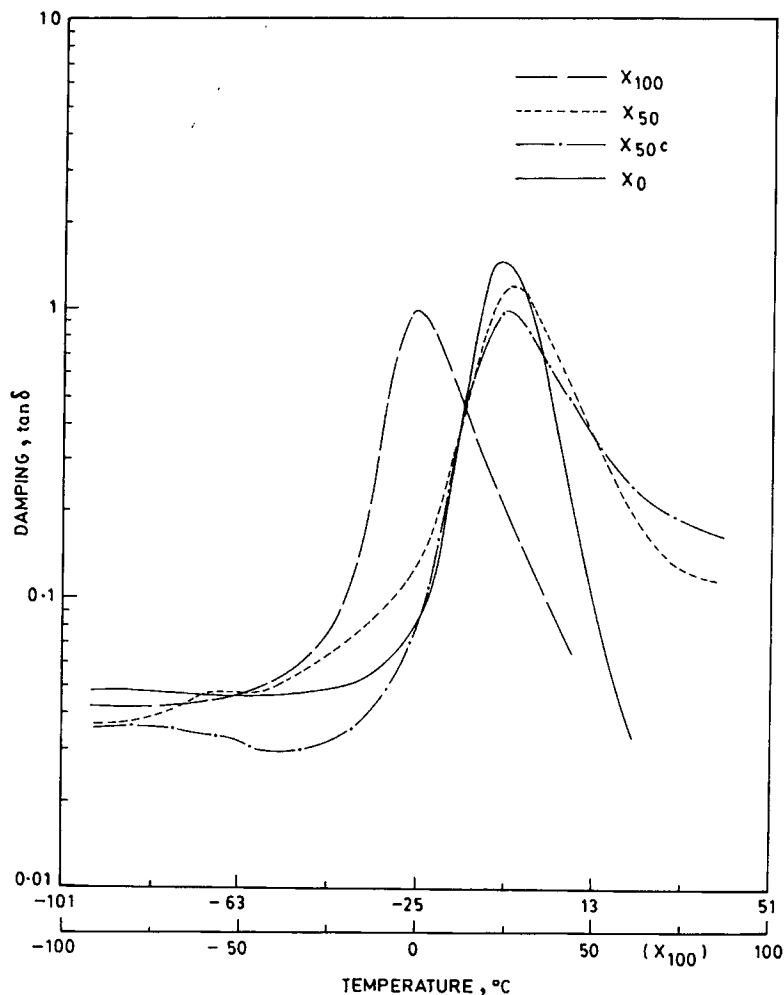


Figure 5 Mechanical damping of hypalon, XNBR, and their blends at different temperatures.

is due to C=O stretching vibration in ester and this band is also detected when a difference spectrum is computed [Fig. 2(d)]. This observation supports the proposed mechanism of reaction between hypalon and XNBR (Fig. 3).

Physical properties of the blend as summarized in Table III indicate that the gum-blend vulcanizate has poor physical properties. However, addition of 20 phr of ISAF black filler increases the tensile strength more than four times, tear resistance about four times, and abrasion resistance more than three times. As expected, addition of reinforcing carbon black increases modulus and hardness and causes reduction in resilience. Higher hysteresis of the filled system (Table IV) causes an increase in heat buildup. When the hysteresis experiment was repeated beyond the first cycle, both hysteresis loss and set in the second and third cycles were less as

compared to the first cycle. Hysteresis plots are shown in Figure 4.

To compare the self-vulcanization system with that of the conventional vulcanizing systems, hypalon and XNBR were vulcanized individually by conventional methods with standard vulcanizing agents. Formulations of the control single rubbers are given in Table I. To eliminate the effect of cross-link density on physical properties, the single systems were vulcanized to the same cross-link density as that of the blend by molding them to the point where the rise in rheometric torque (i.e., the difference between maximum torque and minimum torque) is the same in all the cases. These cure times are given in Table II. A comparison between single rubbers (X_{100} and X_0) and the corresponding blend (X_{50}) indicates that the blend is closer to XNBR vulcanizate (X_{100}) with respect to modulus and ten-

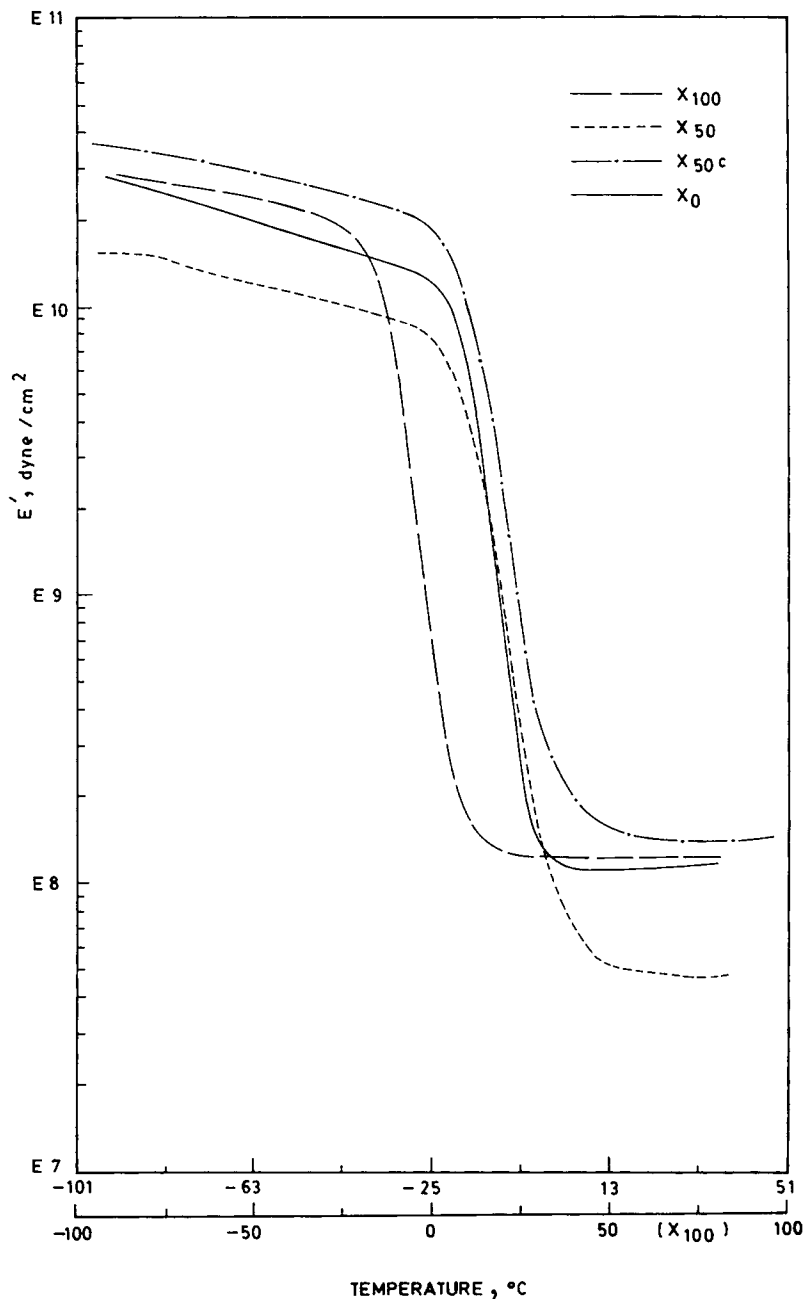


Figure 6 Storage modulus (E') of hypalon, XNBR, and their blends at different temperatures.

sile and tear strength. But the permanent set property of the blend is better than that of XNBR or hypalon vulcanizates. As indicated earlier, both the single rubbers and the blend were of similar cross-link density and, accordingly, the difference in properties are not due to the difference in extent of cross-linking but due to the nature of cross-linking that is a mixture of ionic and covalent for both

hypalon¹⁰ and XNBR¹¹ and covalent (ester) for the blend.

Miscibility of the components in the blend was examined by dynamic mechanical analyses (DMA) and differential scanning calorimetric (DSC) studies. Dynamic storage modulus (E'), loss modulus (E''), and damping ($\tan \delta$) of the blend and single rubbers are shown in Figures 5-7. Dynamic storage

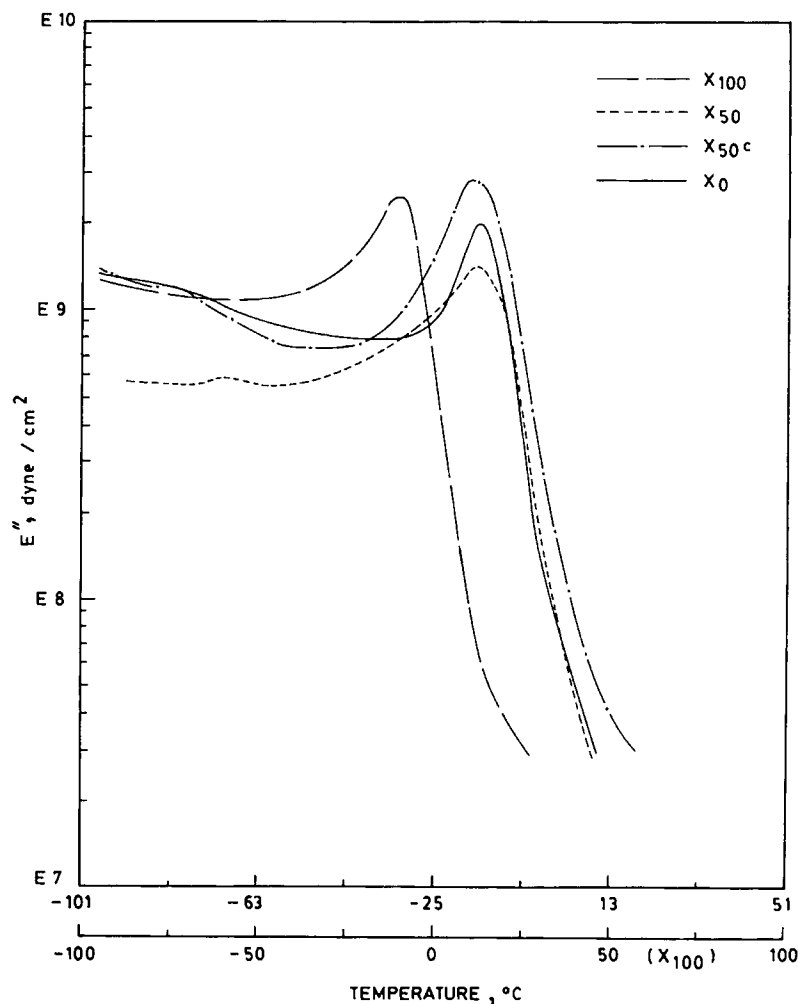


Figure 7 Loss modulus (E'') of hypalon, XNBR, and their blends at different temperatures.

modulus rapidly decreases at the T_g -zone because of the decrease in stiffness of the samples. Concomitantly, loss modulus and damping sharply rise until they attain the maxima and then fall with increase in temperature. The temperature corresponding to the maximum in damping or loss modulus is chosen as the T_g of the samples. Pure hypalon shows α -relaxation corresponding to the glass-rubber transition (T_g) at -7.2°C and XNBR at 0°C . Blends of hypalon and XNBR exhibit only a single T_g at -5.3°C , which occurs in between the T_g 's of the single components, indicating that the system is miscible at the segmental level.

It is apparent from Figure 5 that addition of carbon black filler reduces the glass-rubber transition peak height and also broadens the peak. The reason is bound rubber. Polymer occluded within the in-

ternal void space of the primary structure aggregate of carbon black is not free to fully share in the macroscopic deformation^{12,13} of the polymer. Also, some rubber is adsorbed onto the fillers and loses some of its mobility. Thus, the filled polymers constitute a system with a complex structure of two components; the bound (absorbed and adsorbed) rubber and the bulk rubber. The partly and completely mobilized rubber would cause a perturbed relaxation response, and the property of these layers shifts toward the glassy state. Then, the $\tan \delta$ peak may be ascribed to the glass transition relaxation of the bulk rubber, and, thus, the $\tan \delta$ peak height decreases on addition of carbon black. The broad maxima may be attributed to the superposition of different relaxation processes. DSC studies also support this fact. Figure 8 shows the DSC thermograms of hypalon,

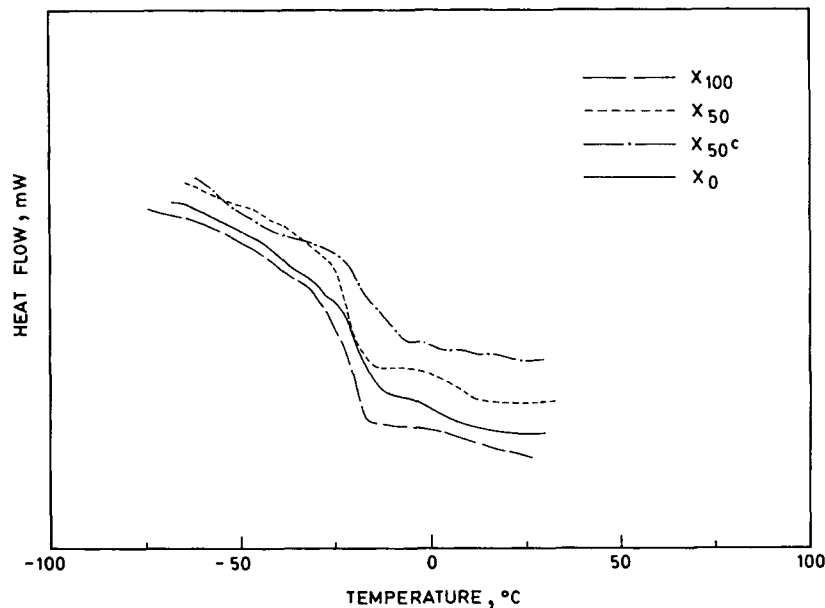


Figure 8 DSC thermogram of hypalon, XNBR, and their blends.

XNBR, and their 50/50 blend (X_{50}). The T_g 's of hypalon and XNBR were detected at -17°C and -23°C , respectively, and that for the blend at -20°C .

The T_g 's of the single components as well as the blends, as obtained from dynamic mechanical analyses and DSC studies, are summarized in Table V.

CONCLUSIONS

The present investigation shows that carboxylated nitrile rubber and hypalon form a miscible blend system that is self-vulcanizable in absence of curatives. The blend can be reinforced by carbon black filler like conventional rubbers. Most of the physical properties are in between the two single rubbers and closer to single XNBR vulcanizate. The permanent

set property of the blend, however, is better than the single-rubber vulcanizates.

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Table V Glass Transition Temperature (T_g 's) as Obtained from Differential Scanning Calorimeter Studies and Dynamic Mechanical Analyses

	T_g ($^\circ\text{C}$)	
	DSC	Mechanical Damping ($\tan \delta$)
X_{100}	-23	0
X_0	-17	-7.2
X_{50}	-20	-5.3
X_{50C}	-20	-5.2