

Self-Vulcanizable Rubber Blend System Based on Neoprene and Carboxylated Nitrile Rubber

SYNOPSIS

A novel rubber blend system has been developed that is self-vulcanizable. No rubber chemical was required for vulcanization, and the mixing operation could be completed in less than 14 min. Such a clean rubber blend system can be reinforced by carbon black filler, and physical properties are comparable to those of conventional rubber vulcanisates. Differential scanning calorimeter studies and dynamic mechanical analysis show that neoprene and carboxylated nitrile rubber are not miscible at the segmental level.

INTRODUCTION

While studying the blend of neoprene and carboxylated nitrile rubber (XNBR), we observed that the blend gets vulcanized during moulding even in the absence of any vulcanizing agent. Since no vulcanizing agent was used, we designate such a system as a "self-vulcanizable rubber blend." In this present communication, we report the results of our preliminary studies on self-vulcanizable neoprene-XNBR blend. Earlier, De and coworkers have reported similar self-vulcanizable rubber blend systems based on XNBR-epoxidized natural rubber^{1,2} and Hypalon-epoxidized natural rubber.^{3,4}

EXPERIMENTAL

Neoprene AC was procured from DuPont Limited. XNBR used was Krynac-221 containing high level of carboxylated monomer and medium high bound acrylonitrile level and was procured from Polysar Limited. Neoprene was first masticated for 2 min on a 14 × 6 in. two-roll mixing mill and was taken out in the form of a sheet. Then XNBR was masticated for 2 min and blended with neoprene for a further period of about 6 min. For the filled system, filler was added to the blend and then mixed thoroughly for a further period of 4 min. Total mixing time was about 10 min for unfilled system and 14 min for the filled system. Rheographs of the blends were taken at 190°C on a Monsanto Rheometer R-100. The blends were vulcanized during moulding at 190°C for 60 min. The following physical properties of the vulcanisates were determined according to the standard methods: Stress-strain (Instron 1195 Universal Testing Machine, ASTM D412-87), tear (In-

stron 1195 Universal Testing Machine, ASTM D624-86), hardness (Shore A, ASTM D2240-86), resilience (Dunlop triptometer, BS:903:Part A8:1963—method A), compression set (ASTM D395-85, method A and method B), heat buildup (Goodrich flexometer, ASTM D623-78), and abrasion resistance (Cryodon-Akron-Dupont abrader, BS:903:Part A9—method C). For swelling studies, the vulcanisates were swollen in chloroform for 48 h and the percent increase in weight due to solvent swelling was noted. Hysteresis experiments were performed on the Instron 1195 Universal Testing Machine at an extension of about 50% of elongation at break. Both chart speed and crosshead speed were 100 mm/min.

Dynamic mechanical properties were measured using Toyo-Baldwin Rheovibron model DDV-III-EP at a strain amplitude of 0.0025 cm and frequencies of 3.5 Hz for XNBR and 11 Hz for neoprene and the blend. The procedure was to cool the sample to -100°C and record the measurements during the warmup. The temperature rise was 1°C/min.

Differential scanning calorimeter (DSC) measurements were run on a Du Pont differential scanning calorimeter model 910 in a nitrogen atmosphere. Glass transition temperatures (T_g 's) of the samples were taken as the midpoint of the step in the scan and run at a heating rate of 20°C/min.

Table I Composition (parts by weight) and Processing Characteristics of Neoprene-XNBR Blend

Blend Designation	A	A _C
Neoprene	100	100
XNBR	100	100
ISAF carbon black	—	40
Mooney viscosity ML ₍₁₊₄₎ at 120°C	31	43
Mooney scorch time at 120°C, min.	> 60	> 60

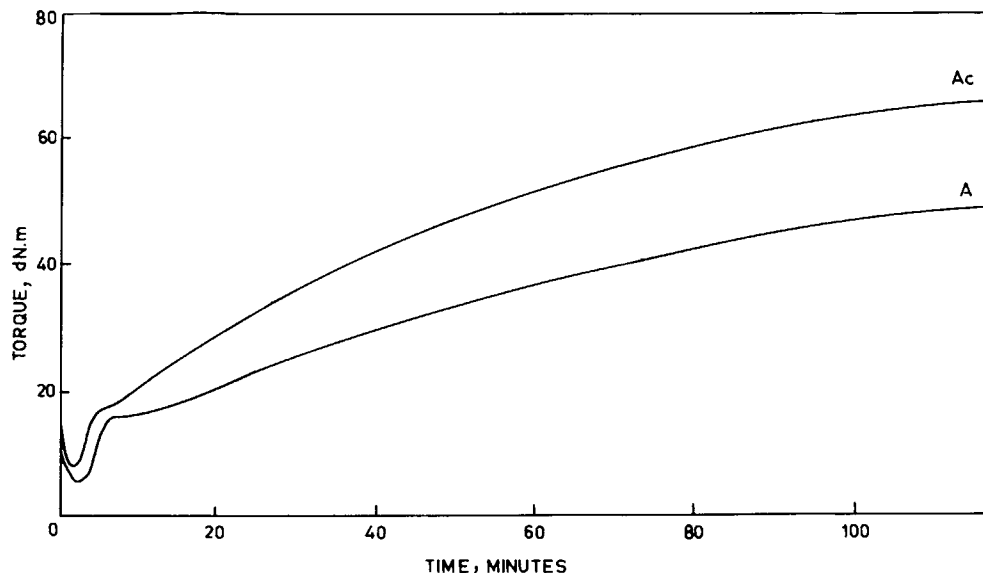


Figure 1 Rheographs of unfilled and ISAF black filled neoprene-XNBR blends at 190°C.

RESULTS AND DISCUSSION

Formulations and the processing characteristics of the two blends are shown in Table I. Blend A contains neoprene/XNBR in the ratio of 1 : 1 (by weight). Blend A_C is similar to blend A, but it contains 20 parts of ISAF carbon black per 100 gm of rubber. Mooney viscosity measurements reveal that the blends are extraordinarily scorch resistant. As expected, addition of reinforcing ISAF carbon black filler increases the Mooney viscosity.

Table II Physical Properties of Neoprene/XNBR Blend Moulded for 60 min at 190°C

Blend	A	A _C
100% modulus (MPa)	0.73	1.32
300% modulus (MPa)	1.21	3.11
Tensile strength (MPa)	3.91	15.95
Elongation at break (%)	900	730
Tear strength (N/mm)	17.27	36.56
Abrasion loss (cm ³ /h)	0.82	0.48
Compression set at constant stress (%)	7	6
Compression set at constant strain (%)	21	16
Heat buildup (ΔT) at 50°C (°C)	26	33
Dynamic set (%)	3	2
Resilience (%)	65	58
Hardness, Shore A	47	55
Swelling in chloroform, percent increase in weight	1120	554

Rheographs of the blend are shown in Figure 1. Increase in rheometer torque with vulcanization time indicates progressive crosslinking of the system. The higher torque values in the case of blend A_C are similar to the conventional rubber system in the sense that reinforcing carbon black increases the torque values due to strong polymer-filler interaction.

Both neoprene and XNBR are soluble in chloroform, but the moulded blend is insoluble in the same solvent. This also indicates that during moulding each blend constituent gets vulcanized by the other. It is evident from Table II that the addition of reinforcing carbon black im-

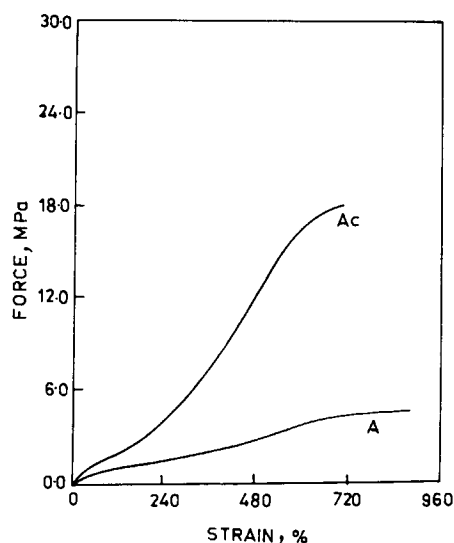


Figure 2 Stress-strain curves of unfilled and ISAF black filled neoprene-XNBR blends.

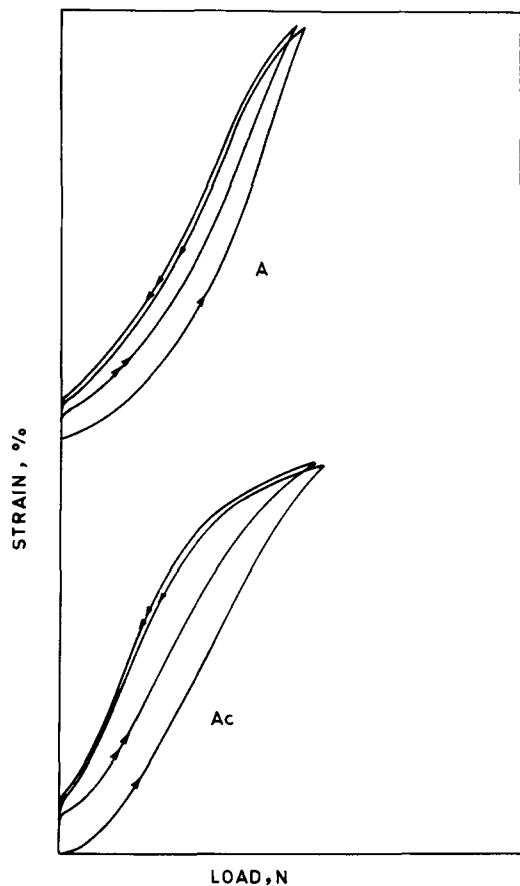


Figure 3 Hysteresis curves of unfilled and ISAF black filled neoprene-XNBR blends at 400 and 350%, respectively.

Table III Hysteresis Behavior of Different Blends

Blend	Cycle	Hysteresis Loss (%)	Set (Arbitrary Units, Instron Chart)
A	1	28	3
	2	12	1
Ac	1	42	5
	2	27	2

Table IV Glass Transition Temperature (T_g 's) as Obtained from DSC Studies and Dynamic Mechanical Analysis

Sample	T_g ($^{\circ}\text{C}$)		
	DSC	Dynamic Mechanical Analysis	Loss Modulus (E'')
Neoprene	-35	-28.1	-33.4
XNBR	-23	0	-4.8
Blend	-38, -15	-32.4, -4.1	-32.4, -12.6

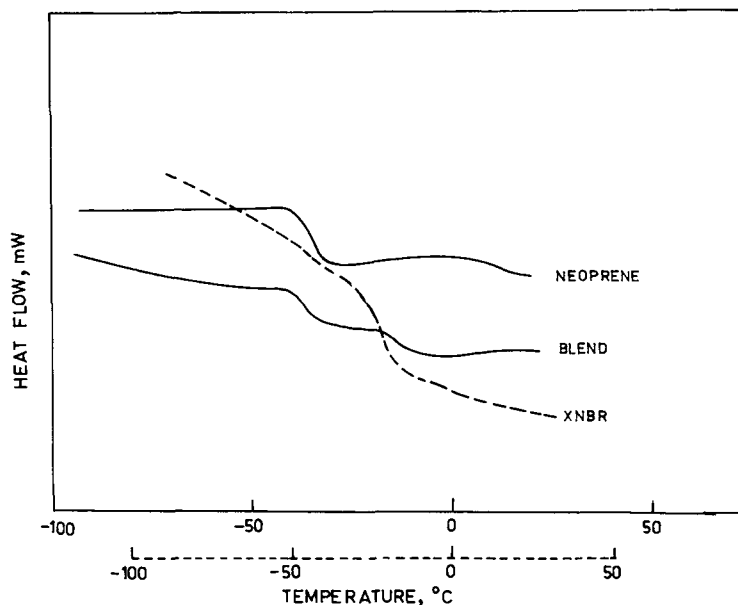


Figure 4 Differential scanning calorimeter thermograms of neoprene, XNBR, and neoprene-XNBR blend.

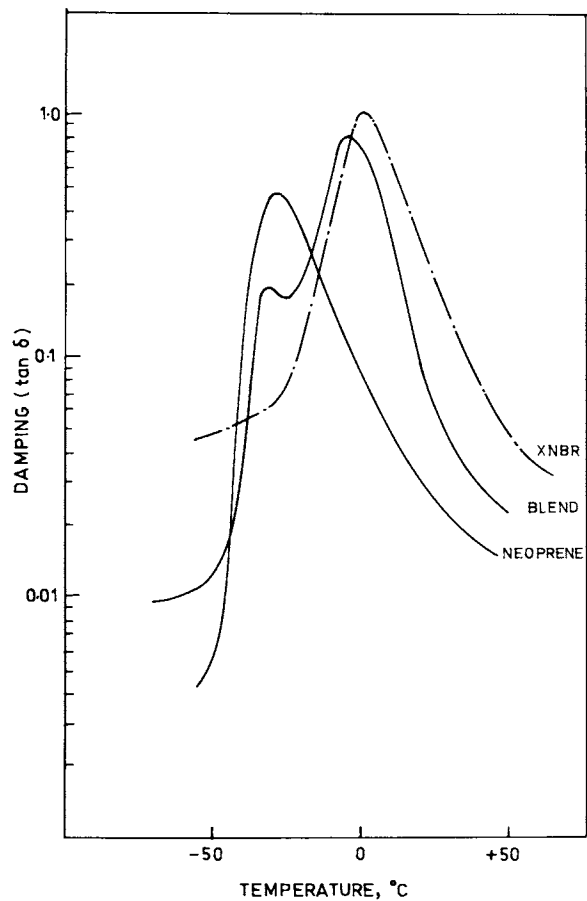


Figure 5 Mechanical damping ($\tan \delta$) of neoprene, XNBR, and neoprene-XNBR blend at different temperatures.

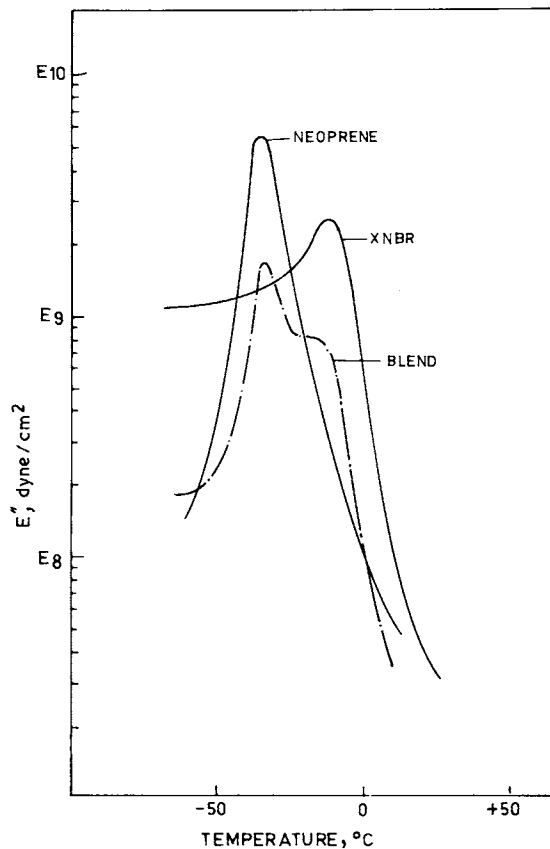


Figure 6 Loss modulus (E'') of neoprene, XNBR, and neoprene-XNBR blend at different temperatures.

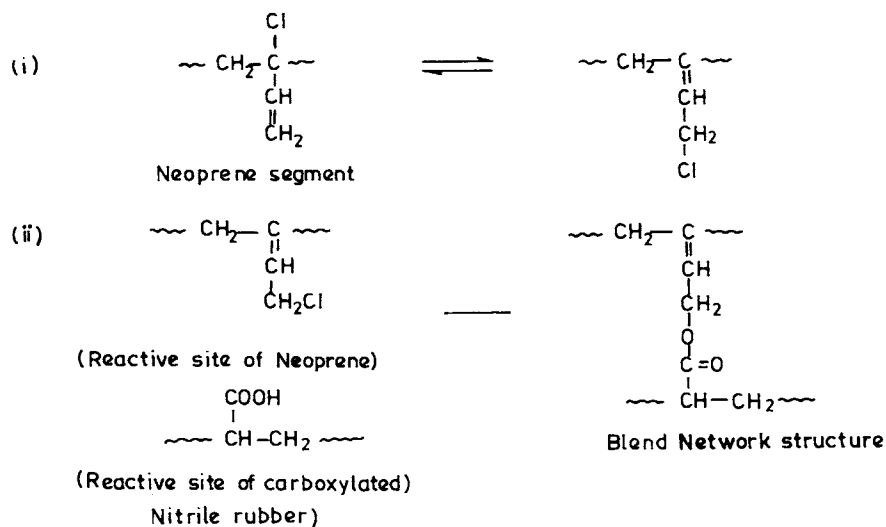


Figure 7 Crosslinking reaction between neoprene and XNBR.

proves the mechanical properties such as tensile and modulus (Fig. 2), tear resistance, and abrasion loss of the blend. On the other hand, it reduces the resilience and increases the heat buildup. Reduction in percent swelling in solvent (chloroform) from 1120% for gum to 554% for the filled system shows increased restriction to solvent swelling due to polymer–filler interaction.

Higher hysteresis of the filled system (Table III) causes increase in heat buildup. When the hysteresis experiment was repeated beyond the first cycle, both hysteresis loss and set in the second cycle were less as compared to the first cycle due to stress softening (Fig. 3).

DSC thermograms of neoprene, XNBR, and the blend are shown in Figure 4. Glass transition of neoprene and XNBR occur at -35 and -23°C , respectively. The blend shows two transitions at -38 and -15°C . The occurrence of two T_g 's in the blend and the shifting of the T_g values away from the values of the individual components indicate that the two components of the blend are not miscible at the segmental level. The results of dynamic mechanical analyses (Figs. 5 and 6) confirm this observation. The blend shows two peaks characteristic of the individual components. Glass transition temperature of the system as determined by differential scanning calorimeter and dynamic mechanical analyses are summarized in Table IV.

In conclusion, neoprene and XNBR form an immiscible blend system that is self-vulcanizable in the absence of

any vulcanizing agent. A probable network structure of the blend vulcanisate is proposed in Figure 7 showing how the reactive allylic $-\text{Cl}$ atom of neoprene reacts with the $-\text{COOH}$ group present in XNBR. This type of rubber blend system is cheap, clean, and requires less energy for processing since no rubber chemicals are used.

References

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