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Self-vulcanizable rubber blend system based on epoxidized natural rubber and chlorosulphonated polyethylene

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A mill-mixed blend of epoxidized natural rubber and chlorosulphonated polyethylene becomes vulcanized during moulding in the absence of any vulcanizing agent. Such a system of self-vulcanizable rubber blend is miscible, as is evident from differential scanning calorimeter studies and dynamic mechanical analysis. The physical properties of the blend are comparable to those of conventional rubber vulcanizates and the blend can be reinforced by carbon black filler.

1. Introduction

Epoxy resin is one of the primary curing agents for chlorosulphonated polyethylene, also known under the trade name "hypalon". It gives water-resistant vulcanizates suitable for coloured products [1]. Accordingly, we thought that hypalon could also be vulcanized by epoxidized natural rubber (ENR). While studying the blend of hypalon and ENR, we found that the blend becomes vulcanized during moulding. In the present article the results of our preliminary studies on the "self vulcanizable" hypalon-ENR blend are reported. Alex *et al.* [2] have previously reported a similar self-vulcanizable rubber blend system based on carboxylated nitrile rubber and epoxidized natural rubber.

2. Experimental procedure

Hypalon 40 used was procured from DuPont Limited, Delaware, USA. The ENR used was ENR-25, with 25 mol % epoxidation (Malaysian Rubber Producers' Research Association, UK) was first masticated in a 14 in. × 6 in. (35.56 cm × 15.24 cm) two roll mixing mill for 4 min. Next hypalon was added and the mixture blended for a further 4 min. To produce a filled compound, filler was added gradually after blending the two rubbers and then mixed thoroughly, again for 4 min.

Rheographs of the blends were taken at 160, 170 and 180° C on a Monsanto Rheometer R-100. The blends were vulcanized at 160° C for 60 min. The following physical properties of the vulcanizates

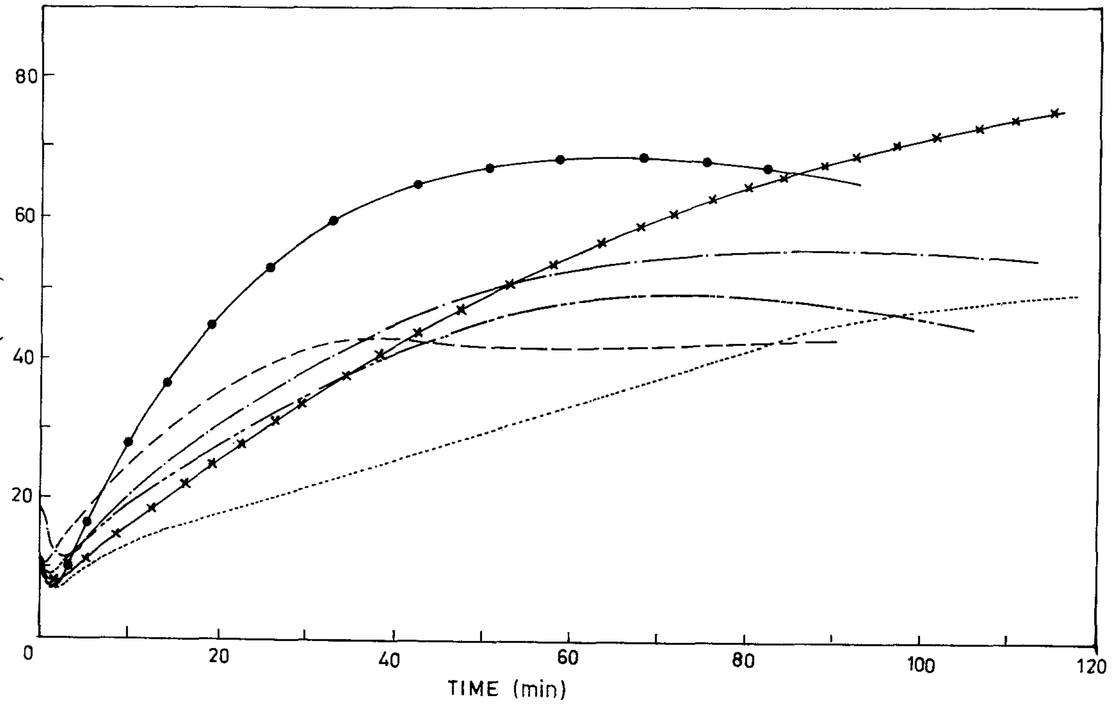

Figure 1 Rheographs of unfilled and ISAF black-filled ENR–hypalon blends at different temperatures. Black: (-●-) 180° C, (- - -) 170° C, (-x-) 160° C. Gum: (– – –) 180° C (–·–) 170° C, (· · · ·) 160° C.

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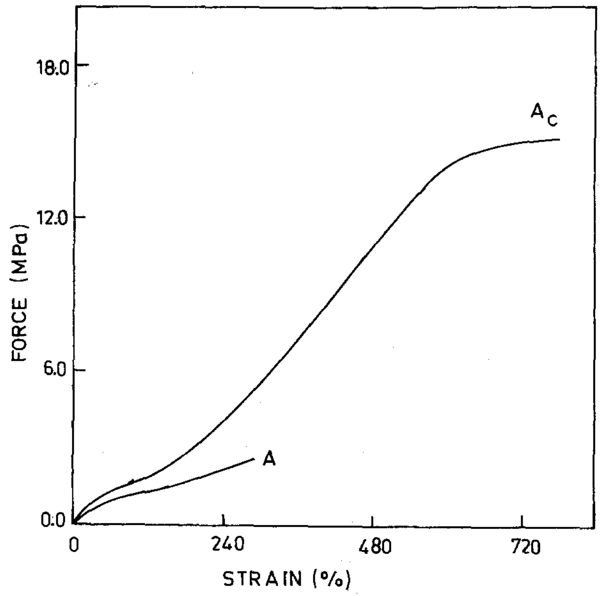

Figure 2 Stress–strain curves of unfilled and ISAF black-filled ENR–hypalon blends.

were determined according to the standard methods: stress–strain (Instron 1195 Universal Testing Machine, ASTM D412-87), tear (Instron 1195 Universal Testing Machine, ASTM D624-86), hardness (Shore A, ASTM D2240-86), resilience (Dunlop tripsometer, BS 903 Part A8: 1963 – method A), compression set (ASTM D395-85 – methods A and B), heat build-up (Goodrich flexometer, ASTM D623-78), fatigue life (Monsanto Fatigue to Failure Tester, ASTM D4482-85) and abrasion resistance (Cryodon Akron Dupont abrader, BS, 903 Part A9: method C). For swelling studies the vulcanizates were swollen in chloroform for 48 h and the per cent increase in weight due to solvent swelling was noted.

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, 11, 35 and 110 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^{-1}.

Differential scanning calorimeter (DSC) studies were done using a Dupont differential scanning calorimeter, model 910 in a nitrogen atmosphere. Glass transition temperatures (T_g) of the sample were taken as the midpoint of the step in the scan, run at a heating rate of 20° C min^{-1}.

Hysteresis experiments were performed in an Instron 1195 Universal Testing Machine at an extension of about 50% of the elongation at break. Both chart speed and cross-head speed were 100 mm min^{-1}.

TABLE I Composition (parts by weight) and processing characteristics of hypalon/ENR-25 blend

	Blend	
	A	A_C
Hypalon	100	100
ENR-25	100	100
ISAF carbon black	–	40
Mooney viscosity $ML_{(1+4)}$ at 120° C	26	26
Mooney scorch time at 120° C (min)	9	8

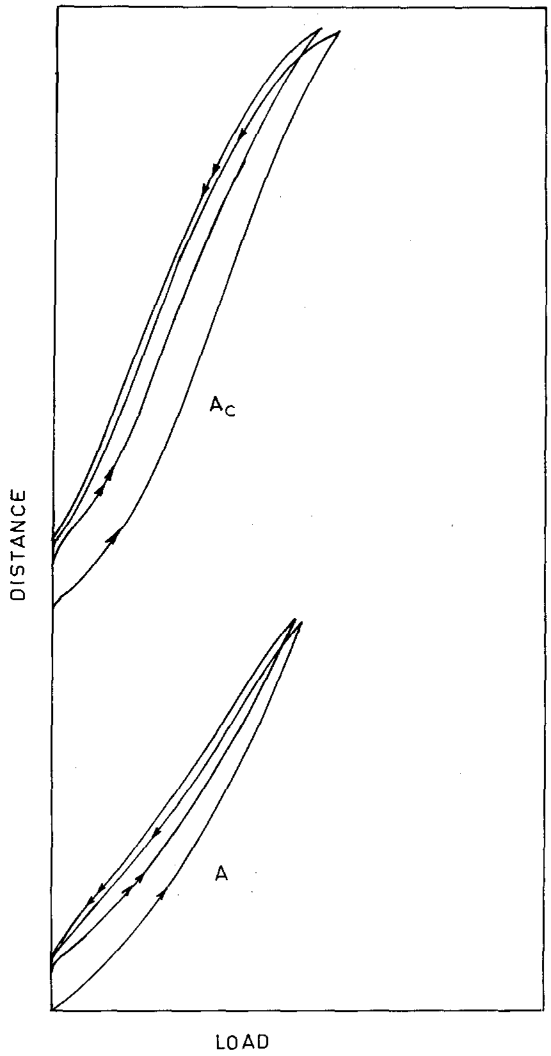

Figure 3 Hysteresis curves of unfilled and ISAF black-filled ENR–hypalon blends at 150% and 400% extension, respectively.

TABLE II Physical properties of hypalon/ENR-25 blend moulded for 60 min at 160° C

	Blend	
	A	A_C
100% modulus (MPa)	0.90	1.20
300% modulus (MPa)	2.34	3.09
Tensile strength (MPa)	2.34	14.32
Elongation at break (%)	300	809
Tear strength (N mm^{-1})	11.68	35.04
Abrasion loss ($\text{cm}^3 \text{h}^{-1}$)	1.23	0.59
Compression set at constant stress (%)	7	6
Compression set at constant strain (%)	38	28
Heat build-up, ΔT (° C)	22*	29
Dynamic set (%)	†	3.55
Resilience (%)	65	57
Hardness, Shore A	53	60
No. of cycles, for fatigue to failure	7300	29000
Swelling in chloroform, (% increase in weight)	980	657

*Value at 11 min.

†Sample failed beyond 11 min.

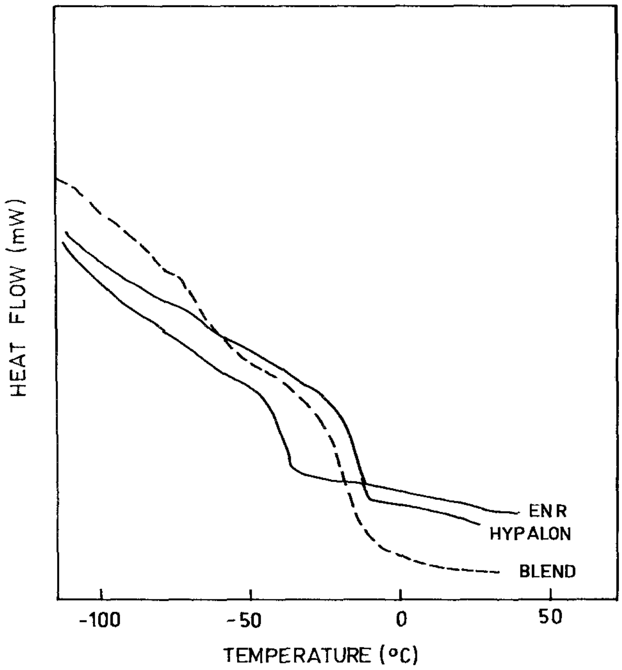

Figure 4 Differential scanning calorimeter thermograms of ENR, hypalon and ENR–hypalon blend.

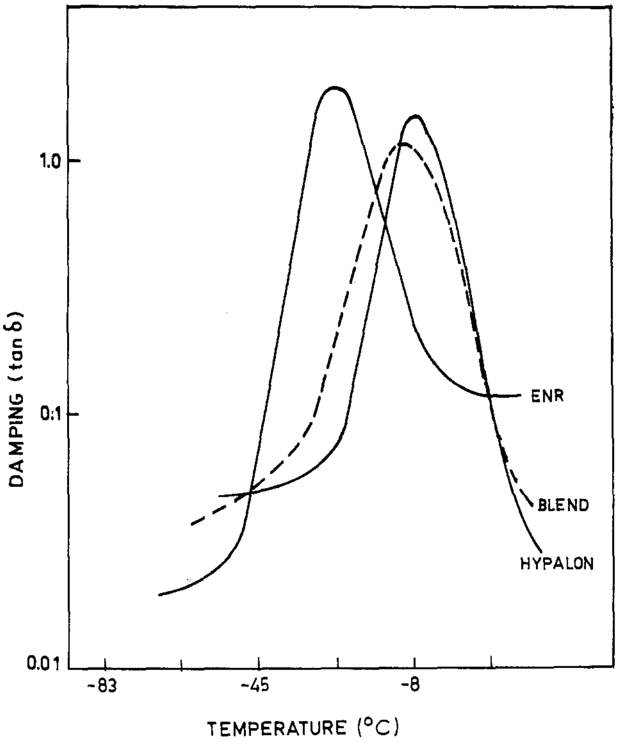

Figure 5 Mechanical damping (tan δ) of ENR, hypalon and ENR–hypalon blend at different temperatures.

3. Results and discussion

Formulations of the two blends and the processing characteristics are shown in Table I. Blend A contains hypalon and ENR in the ratio of 1 : 1 (by weight). Blend A_c is similar to blend A, but it contains ISAF carbon black in the proportion of 20 parts per 100 g rubber.

Rheographs of the blends are shown in Fig. 1. Increase in rheometer torque with vulcanization time indicates progressive cross-linking of the system. Both hypalon and ENR-25 are soluble in chloroform, but the moulded blend is insoluble in the same solvent, which again substantiates the fact that during moulding, each blend constituent becomes vulcanized by the other component. The higher torque values in the case of the carbon black-filled blend at all temperatures indicate strong polymer–filler interaction. The phenomenon is very similar to the conventional rubber systems. Marching increase in modulus with cure time implies that the cure reversion is absent at 160° C even up to 120 min and the vulcanizate network is thermally stable. However, the rheographs at 170 and 180° C show reversion for both unfilled and filled blends.

Physical properties of the moulded blends are shown in Table II. It is evident that the unfilled vulcanizate has poor physical properties. Addition of reinforcing carbon black, however, improves the mechanical properties of the blend. For example, incorporation of reinforcing black filler enhances tensile strength six-fold, tear resistance three-fold, fatigue life four-fold and abrasion resistance two-fold. The stress–strain curves of the unfilled and filled blends are shown in Fig. 2. As expected, addition of carbon black increases the modulus but causes reduction in resilience. Reduction in per cent swelling in solvent (chloroform) from 980% for the gum system to 657% for the filled system shows an increased restriction to solvent swelling due to polymer–filler interaction.

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

DSC thermograms of ENR-25, hypalon and the corresponding blend are shown in Fig. 4. The T_gs of hypalon and ENR-25 were detected at -17 and -41° C while their blend showed the transition at -25° C. A single T_g in the blend occurring between the two individual components indicates complete miscibility of hypalon and ENR-25. Fig. 5 shows the plots of mechanical damping (tan δ) of hypalon,

TABLE III Hysteresis behaviour of the blends

Blend	Cycle no.	Hysteresis loss (%)	Set (arbitrary units, Instron chart)
A	1	24	4
	2	14	2
A_C	1	30	5
	2	16	2

TABLE IV Glass transition temperature (T_g) from DSC studies and dynamic mechanical analysis

Sample	T_g (° C)		
	DSC	Dynamic mechanical analysis (frequency 3.5 Hz)	
		Damping (tan δ)	Loss modulus (E'')
Hypalon	-17	-7.0	-15.3
ENR-25	-41	-25.4	-37.5
Blend A	-25	-9.3	-21.2

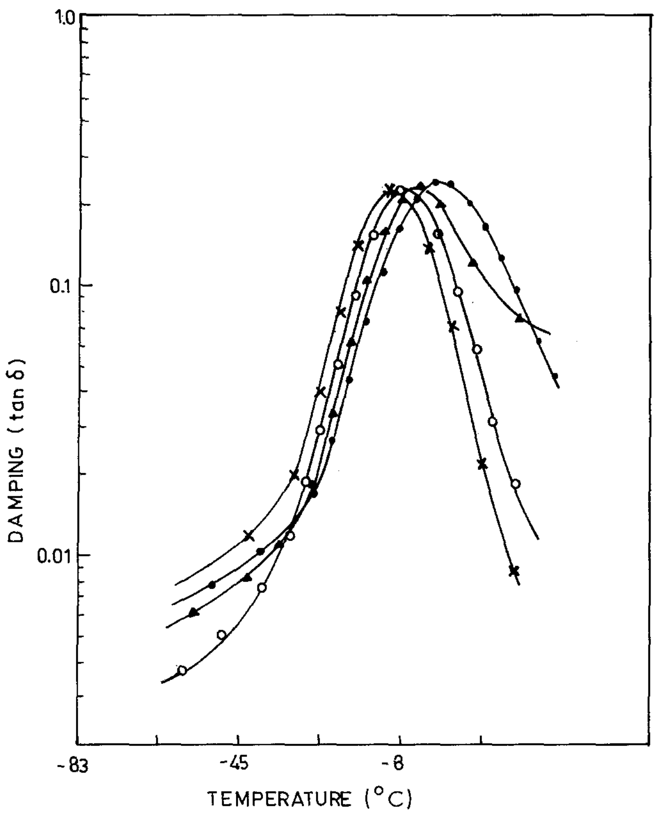

Figure 6 Variation of mechanical damping (tan δ) of ENR–hypalon blend with frequencies at different temperatures: (x) 3.5 Hz, (O) 11 Hz, (▲) 35 Hz, (●) 110 Hz.

ENR-25 and the blend at different temperatures. The blend registers a single peak which occurs between the two single components. Fig. 6 shows the mechanical damping behaviour of the blend at four different frequencies. As expected, the T_g of the blend shifts to higher values at higher frequencies. Figs 7 and 8 show the corresponding plots for loss moduli at different temperatures and different frequencies. Glass transition

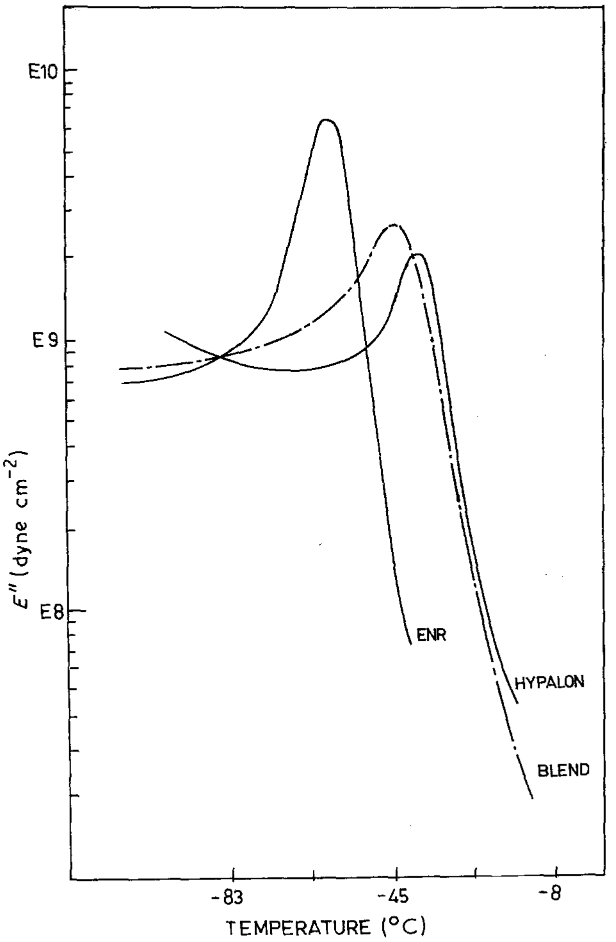

Figure 7 Loss modulus (E'') of ENR, hypalon and ENR–hypalon blend at different temperatures.

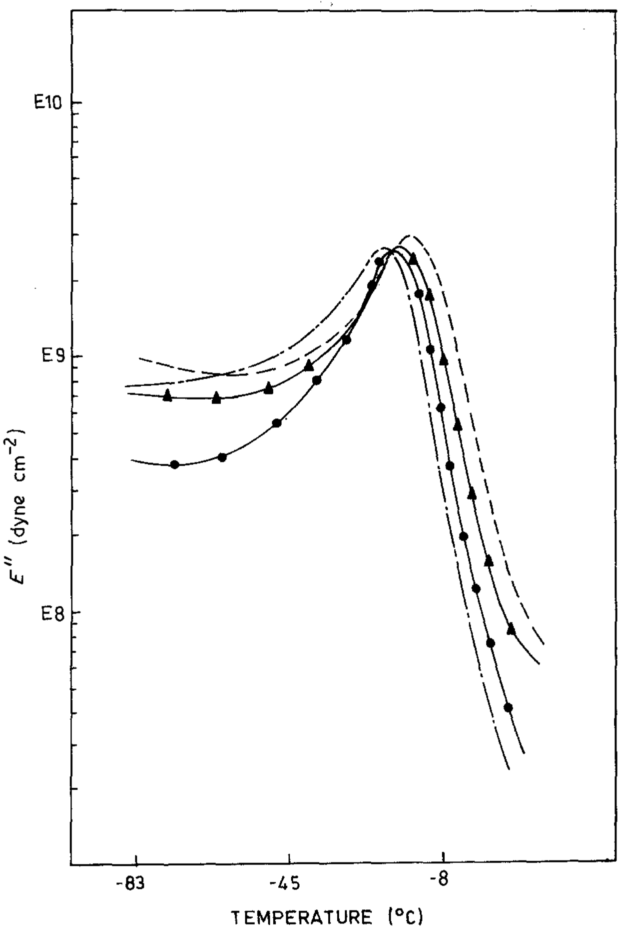

Figure 8 Variation of loss modulus (E'') of ENR–hypalon blend with frequencies at different temperatures. (-●-) 3.5 Hz, (●) 11 Hz, (▲) 35 Hz, (– – –) 110 Hz.

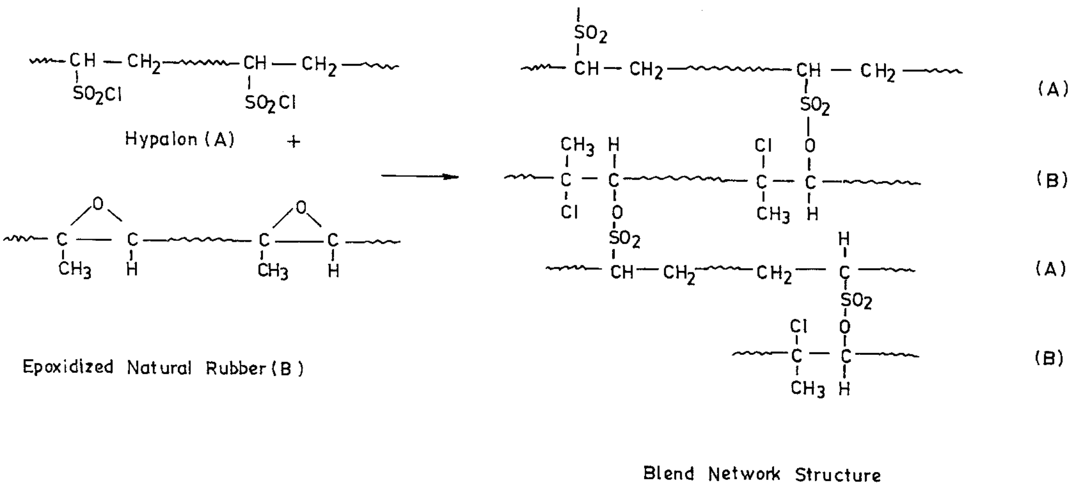

Figure 9 Cross-linking reaction between ENR and hypalon.

temperatures as determined by different methods are summarized in Tables IV and V.

In conclusion, hypalon and ENR-25 form a miscible blend system which is vulcanizable in the absence of any curing agent and registers reinforcement in a black-filled system like conventional rubbers. A probable network structure of the blend vulcanizate is shown in Fig. 7.

TABLE V Glass transition temperature (T_g) of the blend from dynamic mechanical analysis at different frequencies

Frequency (Hz)	T_g (°C)	
	Damping (tan δ)	Loss modulus (E'')
3.5	−9.3	−21.2
11	−6.0	−18.0
35	−2.8	−18.8
110	+0.6	−15.4

References

1. W. HOFMAN "Vulcanization and Vulcanizing Agents" (MacLaren, London, 1967) p. 270.
2. R. ALEX, P. P. DE and S. K. DE, *J. Polym. Sci., Polym. Lett.*, **27** (1989) 361.

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