Self-Vulcanizable Rubber Blend Systems Based on Epoxidized Natural Rubber and Chlorosulfonated Polyethylene: Effect of Blend Composition, Epoxy Content of Epoxidized Natural Rubber, and Reinforcing Black Filler on Physical Properties

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SYNOPSIS

Mill mixed blend of epoxidized natural rubber and chlorosulfonated polyethylene forms a self-vulcanizable rubber blend during molding at high temperatures in absence of any vulcanizing agent, which is confirmed by FTIR studies. The extent of vulcanization reaction not only depends upon time and temperature of molding but also on the level of epoxidation in ENR and its proportion present in the blend. Physical properties of the blends are comparable to that of conventional rubber vulcanizates. Such blends can be reinforced by carbon black filler.

INTRODUCTION

Mill mixed blends of functionally active rubbers can be vulcanized at high temperatures in the absence of any curatives and additives. De and co-workers[1-7] have developed such blends based on: (i) epoxidized natural rubber, hereafter referred to as ENR, and chlorosulfonated polyethylene, hereafter referred to as hypalon; (ii) carboxylated nitrile rubber, abbreviated as XNBR and ENR; (iii) hypalon and XNBR; (iv) neoprene and XNBR; (v) neoprene and ENR. It has been reported earlier that blend of ENR and hypalon gets vulcanized during molding at 160°C in the absence of any vulcanizing agent.[1,6] Miscibility of ENR/hypalon blends depends on blend composition and epoxy content of ENR.[7] Further studies on this system reveals that the extent of crosslinking reaction depends not only upon time and temperature of molding but also on blend composition and extent of epoxy content in epoxidized natural rubber. In the present communication, we report the results of our studies on FTIR spectroscopy and the effect of blend ratio, epoxidation level

in ENR and reinforcing black on physical properties of the blends with special reference to wear behavior.

EXPERIMENTAL

Details of the materials used and formulations of the blends are given in Tables I and II, respectively. The blends are denoted by E_{75}, E_{50}, and E_{25}, the subscripts corresponding to the weight percentage of ENR-50 in the blends. E_0 and E_0' corresponds to 100 wt % of hypalon-40 and E_{100} corresponds to the 100 wt % of ENR-50. Similarly, blends of ENR-25 and hypalon are designated as E_{75}', E_{50}', and E_{25}'. E_{100}' corresponds to the 100 wt % of ENR-25.

Both ENR and hypalon were first masticated separately for about 2 min on a 14 × 6 in. two-roll mixing mill. Then they were blended 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 2°C. For filled compound filler was added gradually after blending the two rubbers and then mixed thoroughly for additional 4 min. The temperature rise in case of filled blends was 5°C. Total mixing time

Table I Details of Materials Used

Materials	Characteristics	Source
Chlorosulfonated polyethylene	Trade name—Hypalon, grade—Hypalon-40	DuPont Ltd.
ENR-50	50 mol % epoxidized natural rubber	The Malaysian Rubber Producers Research Association, Brickendonbury, U.K.
ENR-25	25 mol % epoxidized natural rubber	Malaysian Rubber Producers Research Association, U.K.
Carbon black	ISAF-N 220	Philips Carbon Black Ltd., India

was about 8 min for unfilled and 12 min for filled systems. Table III shows the formulations of the mixes involving control single rubbers, i.e., hypalon (mix no. E_0), ENR-50 (E_{100}), and ENR-25 (E'_{100}). Mixing of compounding ingredients with single rubbers was completed within 9 min for gum mixes and 14 min for filled mixes.

Mooney viscosity and Mooney scorch time were determined at 120°C as per ASTM D1646-1963 by using Negretti automation Mooney shearing disc viscometer, Model MK-III. Rheographs of the mixes were taken at 150°C on a Monsanto rheometer R-100. The blends were cured at 150°C for 60 min. The control mixes were vulcanized to the same extent of crosslinking as that of 50/50 blends of ENR/hypalon by keeping the rise in rheometric torque same. The corresponding cure times for the blend and single rubber mixes are shown in Tables IV and V.

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 D-395-85—method B, where the specimens were subjected to

Table II Formulations of the Blends[a]

	E_{75}	E_{50}	E_{25}	E'_{75}	E'_{50}	E'_{25}
ENR-50	75	50	25	—	—	—
ENR-25	—	—	—	75	50	25
Hypalon	25	50	75	25	50	75

[a] For filled compounds 20 wt % of ISAF carbon black was added and the blends are designated with an added letter C. For example, $E_{50}C$ corresponds to carbon black filled 50/50 blend of ENR-50/hypalon.

compressive deformation for 22 h at 70°C), abrasion resistance (DuPont abrasion tester, BS:903:Part A9: 1957—method C).

The volume fraction of rubber, V_r, in solvent swollen blend was calculated from equilibrium swelling data by the method reported by Ellis and Welding,[8]

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

where T is the weight of the specimen, D is its deswollen weight, F is the weight fraction of insoluble components, and 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 present study.

Infrared spectra of hypalon, ENR-50, and their 1 : 1 blend were taken in the 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 ENR-50 were prepared by molding at 100°C for 2 min, whereas the blend was molded at 180°C for 60 min.

RESULTS AND DISCUSSION

Processing behavior of the blends as measured by Mooney viscometer is shown in Tables IV and V. It has been found that incorporation of hypalon in the blends increases the Mooney viscosity but reduces scorch time. This is more pronounced in case of ENR-50/hypalon blends. The higher viscosity and the lower scorch time for ENR-50/hypalon blends as compared to that of ENR-25/hypalon blends is due to the onset of vulcanization reaction at the test temperature. As expected, ISAF carbon black filler increases Mooney viscosity and reduces scorch time at all blend ratios.

Table III   Formulations of the Single Rubber Mixes

Mix No.	E_{100}	E'_{100}	E_0/E'^d_0	$E_{100}C$	$E'_{100}C$	E_0C/E'_0C
ENR-50	100	—	—	100	—	—
ENR-25	—	100	—	—	100	—
Hypalon	—	—	100	—	—	100
ISAF carbon black	—	—	—	20	20	20
Sodium carbonate	0.25	0.25	—	0.25	0.25	—
Zinc oxide	5	5	—	5	5	—
Magnesium oxide	—	—	10	—	—	10
Stearic acid	2	2	—	2	2	—
Sulphur	2.8	0.3	—	2.8	2.8	—
MOR[a]	1	2.4	—	1	1	—
TMTD[b]	—	1.6	—	—	—	—
Tehone A[c]	—	—	1.5	—	—	1.5

[a] N-oxydiethylene benzothiazole-2-sulfenamide.
[b] Tetramethyl thiuram disulfide.
[c] Dipentamethylene thiuram tetrasulfide.
[d] E_0 corresponds to hypalon mix when it is vulcanized to the same crosslink density as that of 50/50 blend of ENR-50/hypalon. E'_0 corresponds to hypalon mix when it is vulcanized to the same crosslink density as that of 50/50 blend of ENR-25/hypalon.

Table IV   Processing Characteristics of the Mixes

Mix No.	E_{100}	E_{75}	E_{50}	E_{25}	E_0/E'_0	E'_{100}	E'_{75}	E'_{50}	E'_{25}
Mooney viscosity, $ML_{(1+4)}$ at 120°C	6	20	36	80	12	6	11	20	26
Mooney scorch time at 120°C (min)	7	10.5	3.5	2.0	44	6.5	9.0	5.0	4.5
Cure time at 150°C (min)	9	60	60	60	11/6	13	60	60	60

Table V   Effect of ISAF Black Filler on Processing Characteristics of the Mixes

	$E_{100}C$	$E_{75}C$	$E_{50}C$	$E_{25}C$	E_0C/E'_0C	$E'_{100}C$	$E'_{75}C$	$E'_{50}C$	$E'_{25}C$
Mooney viscosity, $ML_{(1+4)}$ at 120°C	8	24	58	90	20	10	14	31	39
Mooney scorch time at 120°C (min)	6	5.0	3.0	2.0	40	6	8.0	3.5	3.5
Cure time at 150°C (min)	11	60	60	60	16/9	5	60	60	60

Rheographs of the blends are shown in Figures 1 and 2. Increase in rheometric torque with vulcanization time indicates progressive crosslinking of the systems. The marching increase in modulus implies that cure reversion is absent and the vulcanizate network is thermally stable at the temperature. It is also evident from the rheographs that the extent of crosslinking reaction depends on the level of epoxidation in ENR and the proportion at which it is present in the blends. The rate as well as state of cure is higher in case of ENR-50/hypalon blends. Again in both ENR-50/hypalon and ENR-25/hy-
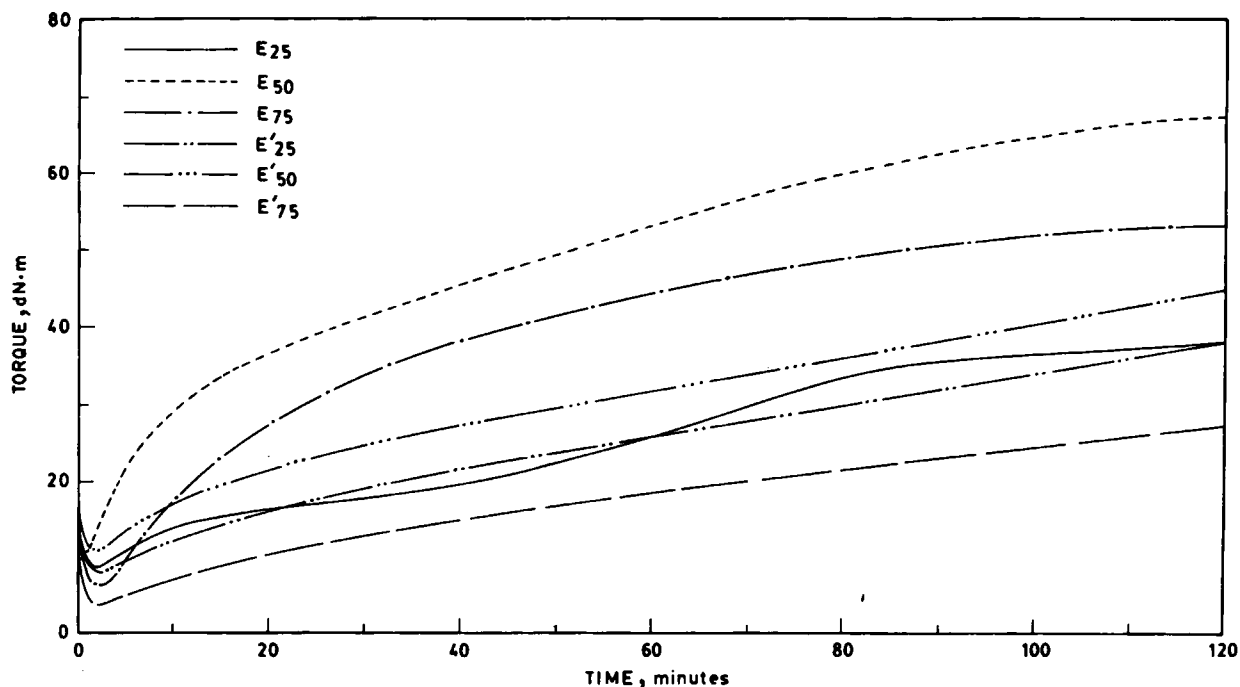
Figure 1   Rheographs of ENR-50/hypalon (E_{75}, E_{50}, and E_{25}) and ENR-25/hypalon (E'_{75}, E'_{50}, and E'_{25}) blends at 150°C.

palon blends, the 50/50 blend ratios, as in blends E_{50} and E'_{50} register maximum torque, indicating maximum extent of reaction. Mechanical properties and V_r, volume fraction of rubber in swollen vul-

canizate, discussed later in this paper, also substantiate this fact. Incorporation of carbon black increases rheometric torque at all blend ratios indicating strong polymer–filler interaction. This
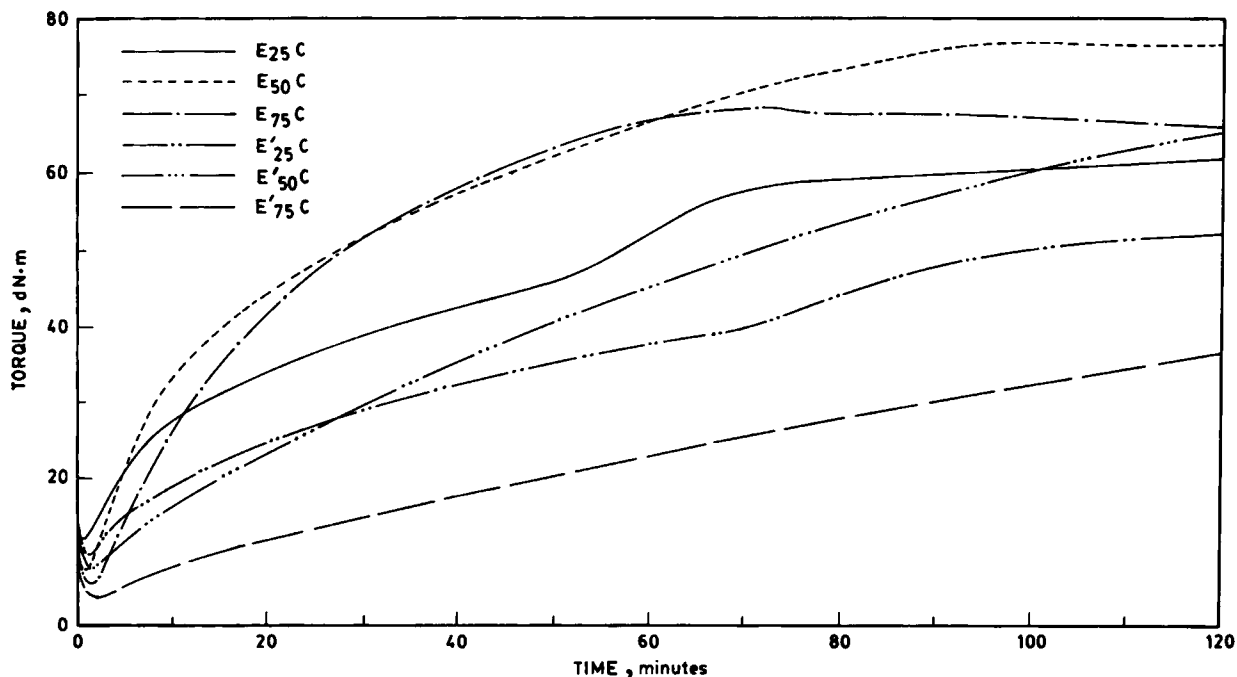
Figure 2   Rheographs of 20 phr of ISAF-black-filled ENR-50/hypalon ($E_{75}C$, $E_{50}C$, $E_{25}C$) and ENR-25/hypalon ($E'_{75}C$, $E'_{50}C$, $E'_{25}C$) blends at 150°C.

Table VI   Effect of Blend Ratio on Physical Properties of ENR/Hypalon Blends

	E_{75}	E_{50}	E_{25}	E'_{75}	E'_{50}	E'_{25}
100% modulus (MPa)	0.61	3.59	1.93	0.39	0.62	0.92
300% modulus (MPa)	1.14	—	5.03	0.75	1.22	1.46
Tensile strength (MPa)	1.97	6.45	6.28	3.45	3.84	3.54
Elongation at break (%)	500	232	511	900	656	663
Tear strength (N/mm)	9.80	13.60	12.10	11.44	13.03	12.90
Abrasion loss (cc/h)	2.5	0.5	0.54	22.4	1.7	0.3
Compression set at						
(a) constant stress (%)	4	10	a	10	15	35
(b) constant strain (%)	15	30	a	28	37	80
Resilience (%)	46	21	30	40	46	43
Hardness (Shore A)	40	67	53	32	42	39
V_r, volume fraction of rubber						
in swollen vulcanizate	0.11	0.15	0.05	0.07	0.09	0.08

a Sample could not be molded.

phenomenon is very similar to that of conventional rubber systems.

Physical properties of the blends are given in Tables VI and VII. On comparison of mixes having high epoxy content (mixes E_{75}, E_{50}, and E_{25}) with those of low epoxy content (mixes E'_{75}, E'_{50}, and E'_{25}), it has been found that the former mixes have higher modulus, higher hardness, better abrasion resistance, and lower elongation at break, which indicates higher extent of crosslinking. As noted earlier, the extent of crosslinking reaction is also dependent upon blend composition, e.g., maximum reaction occurs in the 50/50 blends and the same is reflected in physical properties.

The difference in deformation characteristics of the blends under uniaxial tensile stress is shown in

Figures 3 and 4. ENR-rich blends (i.e., E_{75} and E'_{75}) exhibit viscoelastic deformation of a very soft rubber and break at high strain. The 50/50 blend of ENR-50/hypalon (E_{50}) registers minimum elongation but highest tensile strength due to maximum extent of crosslinking. It shows a linear viscoelastic deformation where energy is stored in reversible manner up to a strain of 6% beyond which irreversible viscoelastic deformation is observed. Although the crosslink density of 75/25 blend is higher than 25/75 blend of ENR-50/hypalon, tensile strength is lower in the former case. This can be explained by high gum strength of hypalon over ENR-50 (Table VIII). There is not much change in tensile strength for the blends of ENR-25/hypalon. But elongation at break is found to be min-

Table VII   Effect of ISAF Black Filler on the Physical Properties of the ENR/Hypalon Blends

|	$E_{75}C$	$E_{50}C$	$E_{25}C$	$E'_{75}C$	$E'_{50}C$	$E'_{25}C$
100% modulus (MPa)	1.48	3.00	4.52	1.09	1.33	2.49
300% modulus (MPa)	6.82	12.27	11.81	3.85	4.05	7.30
Tensile strength (MPa)	9.42	15.30	12.98	9.46	12.69	8.70
Elongation at break (%)	356	338	367	525	835	445
Tear strength (N/mm)	25.00	25.70	17.60	24.80	36.50	31.30
Abrasion loss (cc/h)	2.2	0.5	0.5	1.9	1.1	0.2
Compression set at						
(a) constant stress (%)	3	11	17	5	15	20
(b) constant strain (%)	14	30	65	28	36	53
Resilience (%)	32	19	17	27	43	34
Hardness (Shore A)	51	67	75	45	47	62
V_r, volume fraction of rubber						
in swollen vulcanizate	0.13	0.18	0.14	0.14	0.17	0.16
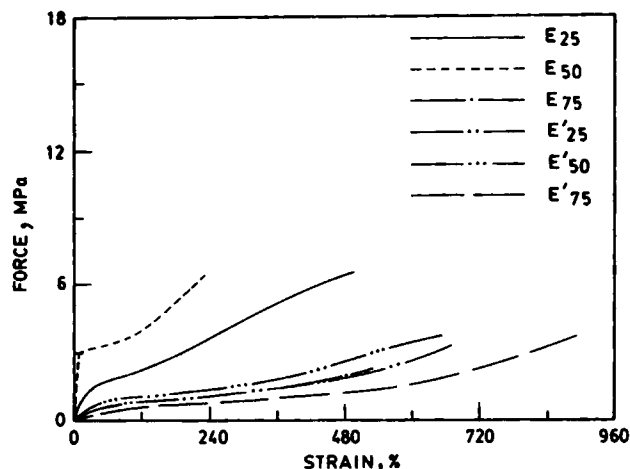
Figure 3 Stress–strain behavior of ENR-50/hypalon and ENR-25/hypalon blends.

imum for 50/50 blend and all these blends show viscoelastic deformation of very soft rubber. Incorporation of ISAF carbon black filler causes several-fold increase in both modulus and tensile strength of the blends due to strong polymer–filler interaction. It is also found that addition of filler increases elongation at break for the 50/50 blends whereas for others it is decreased.

Tear strength is found to be maximum for the 50/50 blends of ENR/hypalon. The effect of epoxidation level is not significant on tear strength of

the blends. Expectedly incorporation of carbon black enhances tear strength.

Compression set results show that with increase in hypalon content in the blends, compression set increases. It is reported that hypalon of standard formulation has higher set than that of other elastomers.[9] On comparison of the blend of ENR-50/hypalon with that of ENR-25/hypalon, the former shows better set properties than the latter. This is due to higher crosslink density in ENR-50/hypalon blends as set is inversely proportional to the number of crosslinks.[10] Another interesting observation is that reinforcing filler like ISAF black has little effect on ENR-rich blends, whereas hypalon-rich blends (E_{25} and E'_{25}) are greatly affected by the filler.

Resilience of the blends depends on blend composition as well as on the level of epoxidation in ENR. For example, ENR-25/hypalon blends are more resilient than that of ENR-50/hypalon blends. It is not clearly understood why 50/50 blend of ENR-25/hypalon shows maximum resilience, but the 50/50 blend of ENR-50/hypalon shows low resilience. As expected, incorporation of carbon black reduces the resilience of the blends.

In general, hardness increases as the hypalon content in the blend increases and it is maximum for 50/50 blends. Because of higher crosslink density ENR-50/hypalon blends have higher hardness as compared to ENR-25/hypalon blends. Addition of carbon black increases hardness in all cases, but the increase is less pronounced in the 50/50 blends.
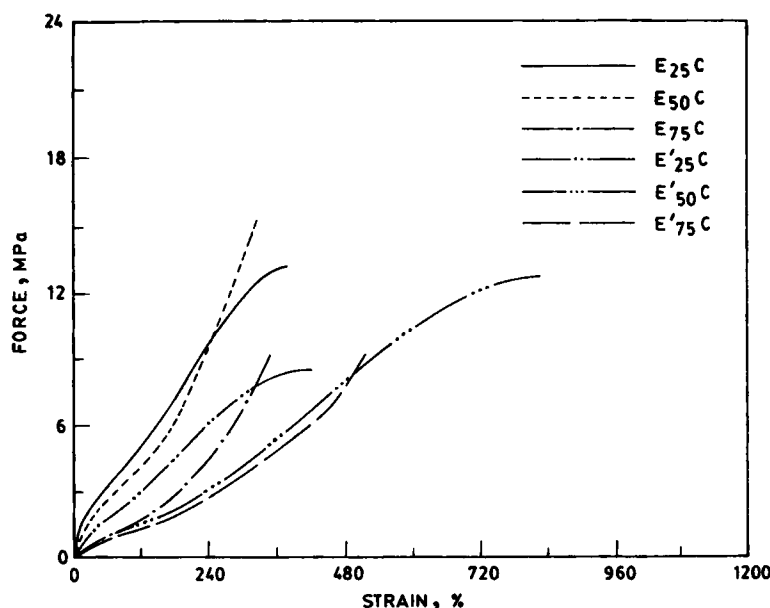

Figure 4 Stress–strain behavior of 20 phr ISAF-black-filled ENR-50/hypalon and ENR-25/hypalon blends.

Table VIII   Physical Properties of Vulcanizates of ENR-50, Hypalon, and Their 50 : 50 Blend

	E_{100}	E_{50}	E_0	$E_{100}C$	$E_{50}C$	E_0C
Modulus, 100% (MPa)	0.93	3.59	1.41	1.44	3.00	2.86
300% (MPa)	2.25	—	3.49	4.42	12.27	11.80
Tensile strength (MPa)	3.55	6.45	12.12	18.49	15.30	22.46
Elongation at break (%)	430	232	676	694	338	500
Tear strength (N/mm)	26.30	13.60	23.50	32.70	25.70	35.30
Abrasion loss (cc/h)	14	0.5	0.2	1.2	0.5	0.2
Compression set at						
(a) constant stress (%)	14	10	16	11	11	9
(b) constant strain (%)	51	30	53	48	30	42
Resilience (%)	56	21	46	42	19	43
Hardness (Shore A)	40	67	56	55	67	67
V_r	0.15	0.15	0.15	0.18	0.18	0.18

The effect of blend ratio, level of epoxidation in ENR, and reinforcing black filler is most prominent in case of abrasion resistance. With increase in hypalon content in the blend, the abrasion resistance increases. Again abrasion resistance is better with ENR-50/hypalon blends as compared to ENR-25/ hypalon blend. But at high hypalon content the abrasion resistance of both blends (E_{25} and E'_{25}) is similar and the behavior approaches to that of control single hypalon vulcanizate (Tables VIII and IX). In order to understand the mechanism of abrasion, we have analyzed SEM fractographs of the abraded surfaces. In abrasion mechanical, chemical, and thermal processes are involved.[11] High abrasion resistance is observed in vulcanizates with high hardness, modulus, tensile strength, tear strength, resistance to thermooxidative degradation, and crack growth resistance under dynamic conditions.[12] Such elastomeric vulcanizates show ridge formation during abrasion.[13,14]

Figures 5 and 6 show the SEM photomicrographs of abraded surface of control ENR-25 and ENR-50 vulcanizates. In both ENR-25 and ENR-50, abrasion resistance is very poor (Tables VIII and IX) and the material seems to be chipped off by the abrasive. This is due to low matrix strength as seen from tensile properties and hardness (Tables VIII and IX). The rubber is removed in lumps by the abrasive. When filler is incorporated, abrasion resistance is improved (Figs. 7 and 8) due to high matrix strength caused by polymer–filler interaction.

Control hypalon vulcanizate shows excellent abrasion resistance because of its high matrix strength and the abrasion resistance is not affected by presence of reinforcing filler (Table VIII). The failure surface of hypalon after an abrasion period of 10 min shows parallel abrasion channels (Fig. 9). Careful examination of the failure surface reveals the development of microridges over the worn surface. It shows low ridge height and close spacing of

Table IX   Physical Properties of Vulcanizates of ENR-25, Hypalon, and Their 50 : 50 Blend

|	E'_{100}	E'_{50}	E'_0	$E'_{100}C$	$E'_{50}C$	E'_0C
100% Modulus (MPa)	0.41	0.62	1.23	1.20	1.33	2.30
300% Modulus (MPa)	0.75	1.22	3.10	3.78	4.05	8.46
Tensile strength (MPa)	3.35	3.84	11.31	21.60	12.69	17.40
Elongation at break (%)	960	656	676	787	835	573
Tear strength (N/mm)	11.50	13.03	20.80	35.00	36.50	37.00
Abrasion loss (cc/h)	23	1.7	0.2	1.0	1.1	0.2
Compression set at						
(a) constant stress (%)	14	15	34	6	15	26
(b) constant strain (%)	25	37	62	28	36	54
Resilience (%)	55	46	45	40	43	43
Hardness (Shore A)	15	42	52	50	47	65
V_r	0.09	0.09	0.09	0.17	0.17	0.17
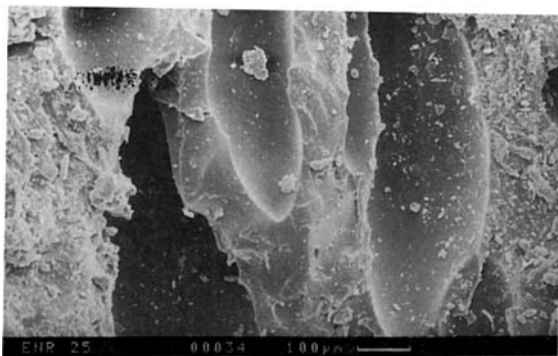
Figure 5   SEM fractograph of the abraded surface of ENR-25 vulcanizate.
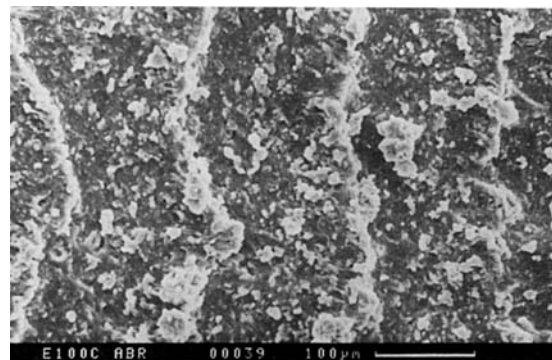

Figure 8   SEM fractograph of the abraded surface of 20 phr of ISAF-black-filled ENR-50 vulcanizate.
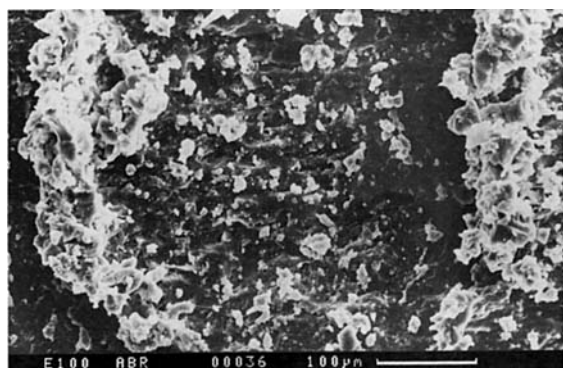

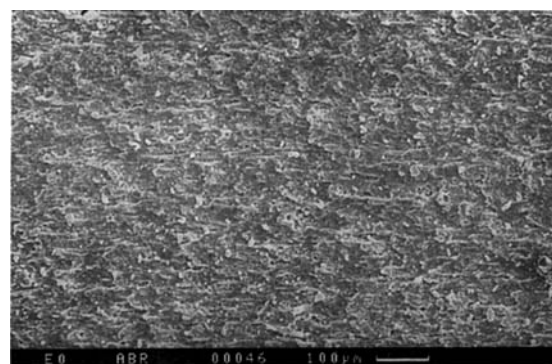**Figure 6**   SEM fractograph of the abraded surface of ENR-50 vulcanizate.

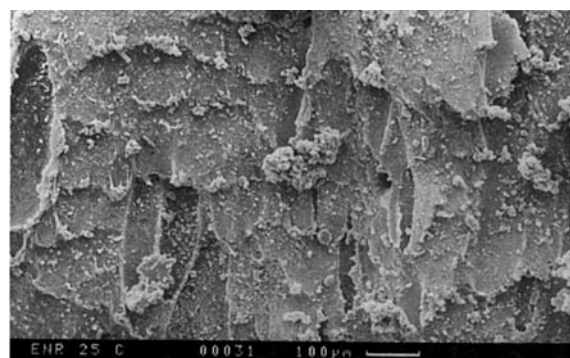**Figure 9**   SEM fractograph of abraded surface of hypalon vulcanizate.

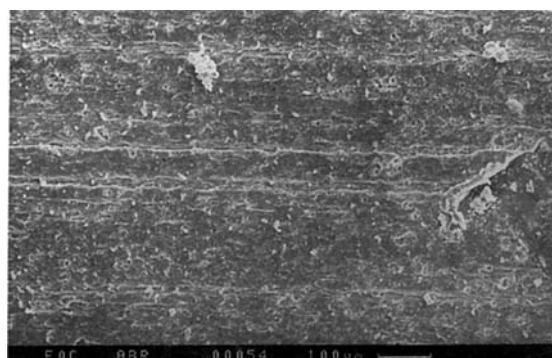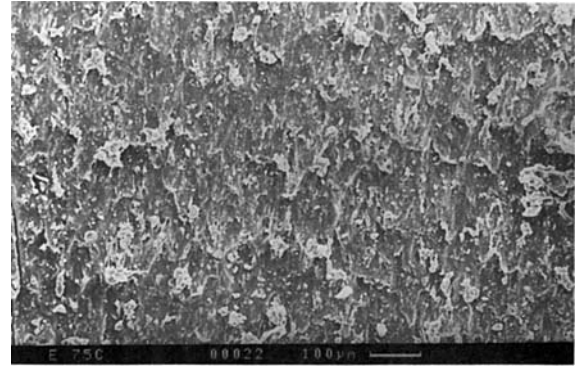**Figure 7**   SEM fractograph of the abraded surface of 20 phr of ISAF-black-filled ENR-25 vulcanizate.

Figure 10   SEM fractograph of the abraded surface of ISAF black-filled hypalon vulcanizate.

the ridges, which are indicative of high resistance to abrasion.[15] On addition of carbon black, fully developed closely spaced microridges are formed in the direction perpendicular to the direction of abrasion (Fig. 10), showing frictional type of wear.[16]

Blending with ENR lowers the abrasion resistance of hypalon as ENR shows poor abrasion re-

sistance. Figures 11–13 show the abraded surfaces of the blends of ENR-50 and hypalon. The tensile and tear strength of the blends were in the order $E_{25} \simeq E_{50} > E_{75}$ (Table VI). Thus the higher mechanical properties of E_{25} and E_{50} blends account for their higher abrasion resistance compared to E_{75}. Both E_{25} and E_{50} show ridge formation and follow abrasive
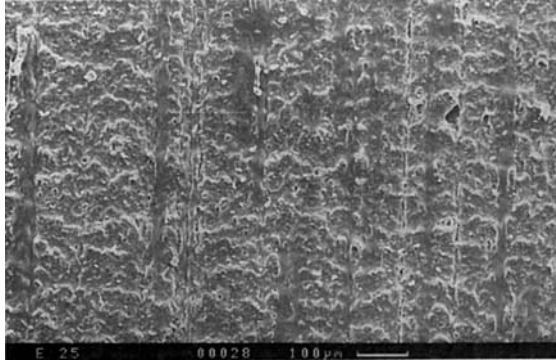
Figure 11   SEM fractograph of the abraded surface of 25/75 blend of ENR-50/hypalon.

Figure 12   SEM fractograph of the abraded surface of 50/50 blend of ENR-50/hypalon.

Figure 13   SEM fractograph of the abraded surface of 75/25 blend of ENR-50/hypalon.

Figure 14   SEM fractograph of the abraded surface of 20 phr of ISAF-black-filled 75/25 blend of ENR-50/hypalon.
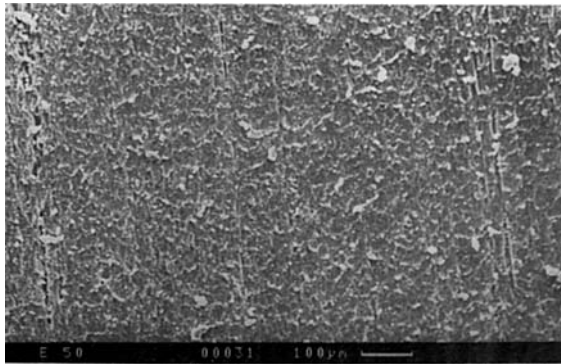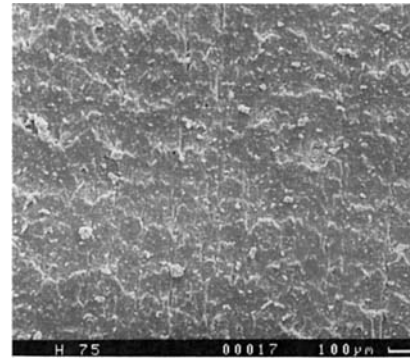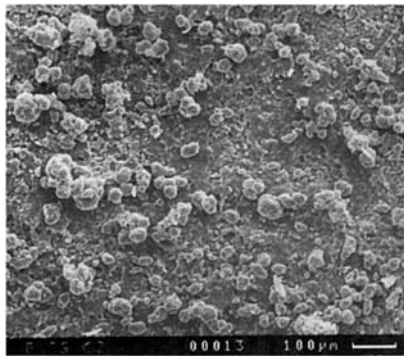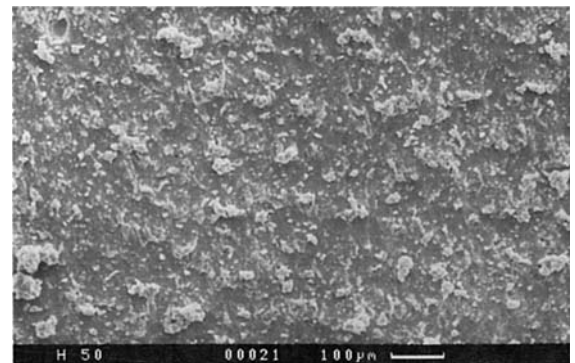

Figure 15   SEM fractograph of the abraded surface of 25/75 blend of ENR-25/hypalon.

Figure 16   SEM fractograph of the abraded surface of 50/50 blend of ENR-25/hypalon.

type of wear. On addition of 20 parts of ISAF carbon black, the mechanism of wear changes from abrasion to frictional for E_{50} blend. There is no significant change in abrasion resistance of E_{50} and E_{25} on addition of filler.

In the case of E_{75}, the pattern is not developed and some sort of ball formation is observed. The material seems to be chipped off by the abrasive due to the low matrix strength. However, incorporation of carbon black improves the abrasion resistance of the blend due to the improved matrix strength (Fig. 14).

Figures 15–17 show the wear surface of ENR-25/hypalon blends. E'_{25} shows ridge formation parallel
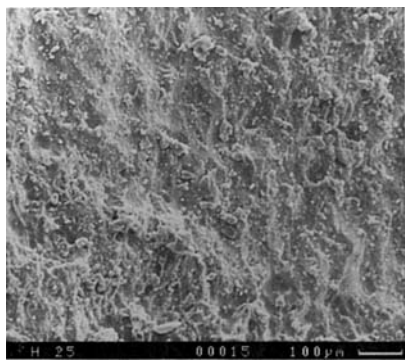
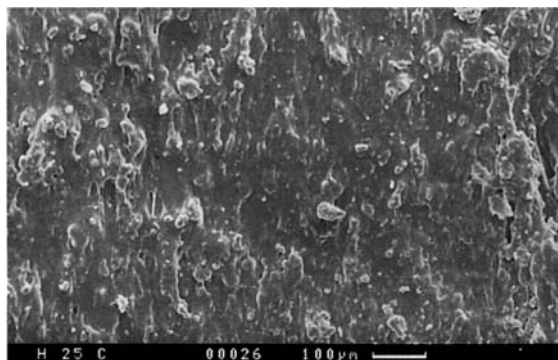**Figure 17** SEM fractograph of the abraded surface of 75/25 blend of ENR-25/hypalon.

Figure 18 SEM fractograph of the abraded surface of 20 phr of ISAF-black-filled 75/25 blend of ENR-25/hypalon.

to the direction of abrasion (Fig. 15). The low ridge height and close spacing indicates high abrasion resistance.[15] Addition of carbon black again lowers the ridge height and causes closer spacing of the ridges. E'_{50} shows moderate abrasion resistance. The abrasion pattern is less defined. Here material removal

occurs in small lumps (Fig. 16). As expected, reinforcing black filled vulcanizates shows lower abrasion loss and follows abrasive type of wear mechanism. In case of E'_{75}, the ridges are not continuous and do not form a well-defined pattern of abrasion during the test. Deformation of the ridges is clearly
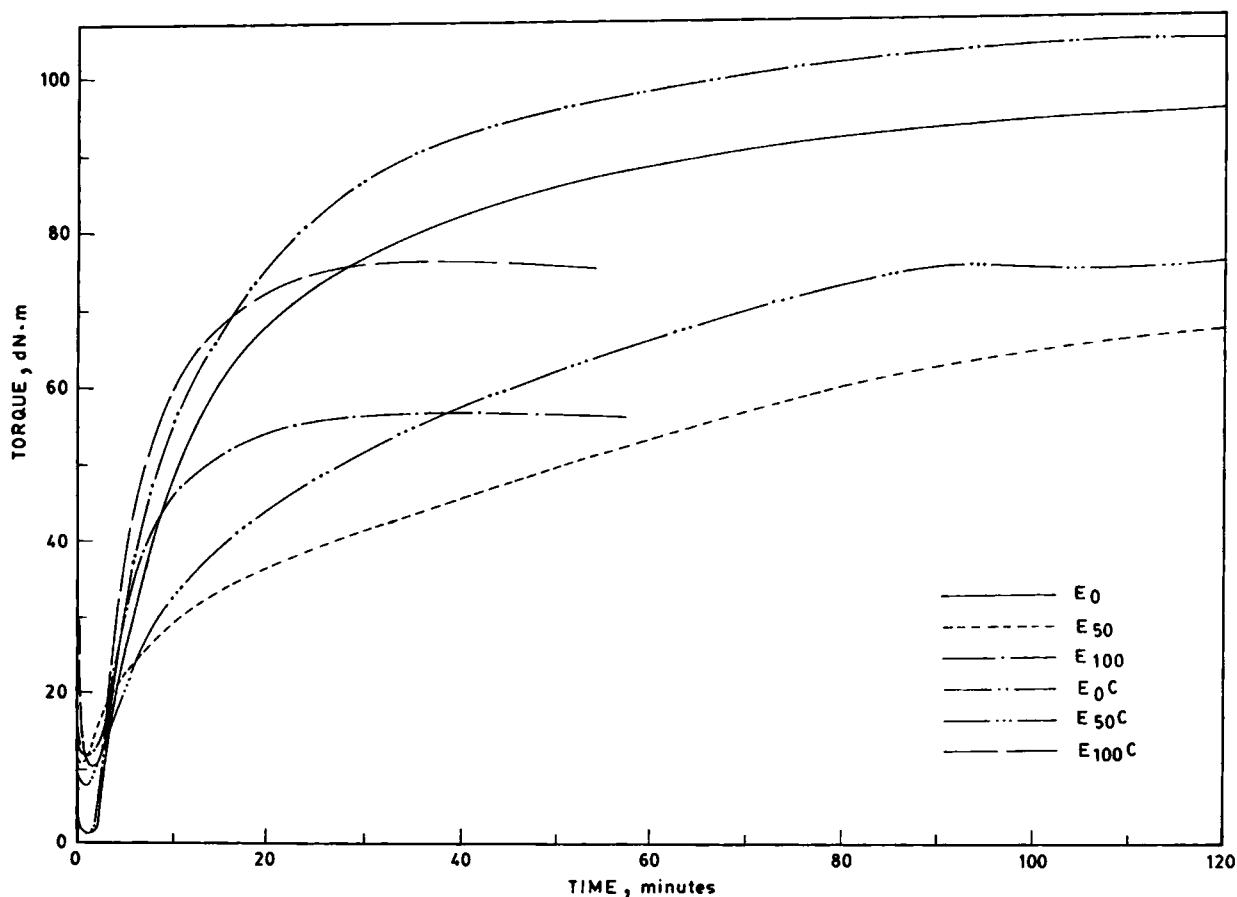

Figure 19 Rheograph of ENR-50, hypalon, and their 1 : 1 blend at 150°C (both gum and 20 phr of ISAF black filled).
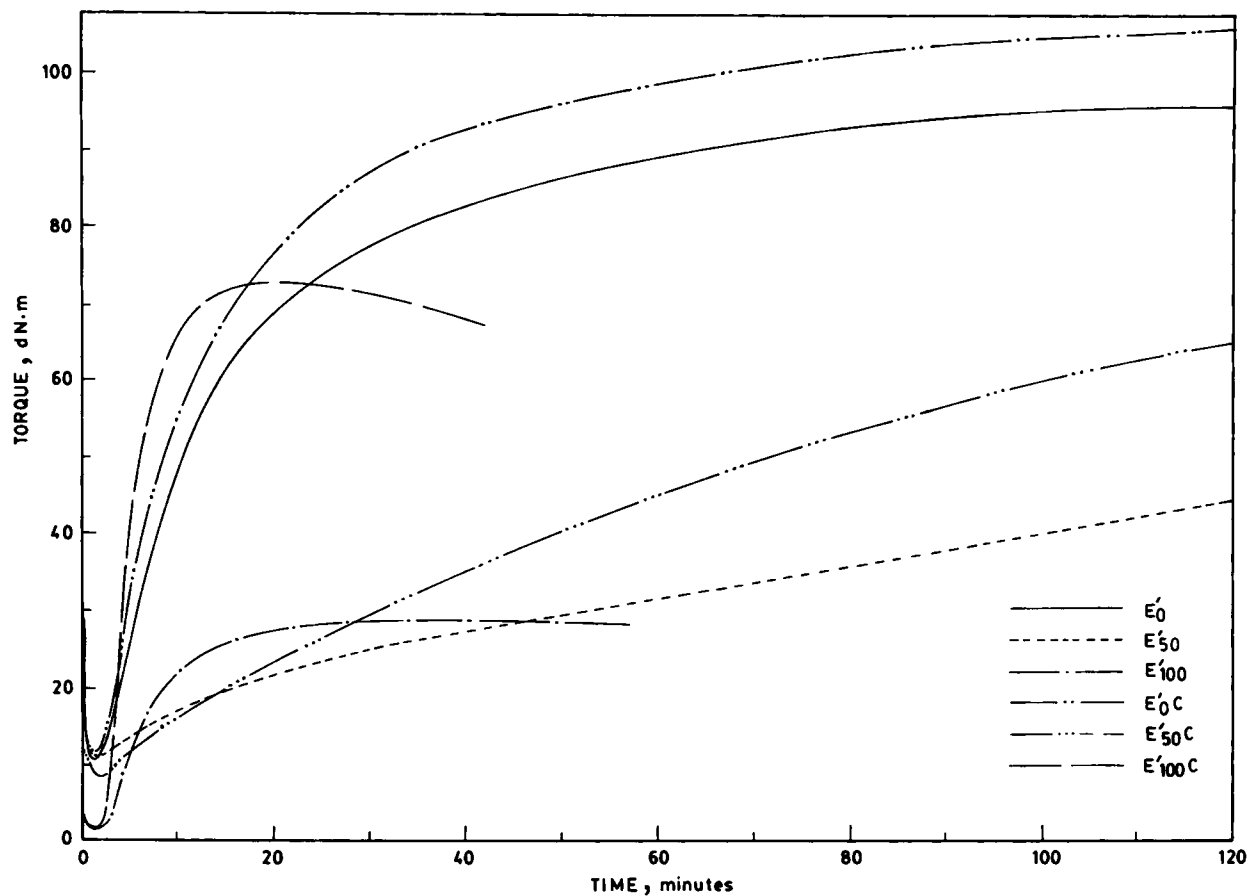
Figure 20   Rheograph of ENR-25, hypalon, and their 1 : 1 blend at 150°C (both gum and 20 phr of ISAF-black-filled).
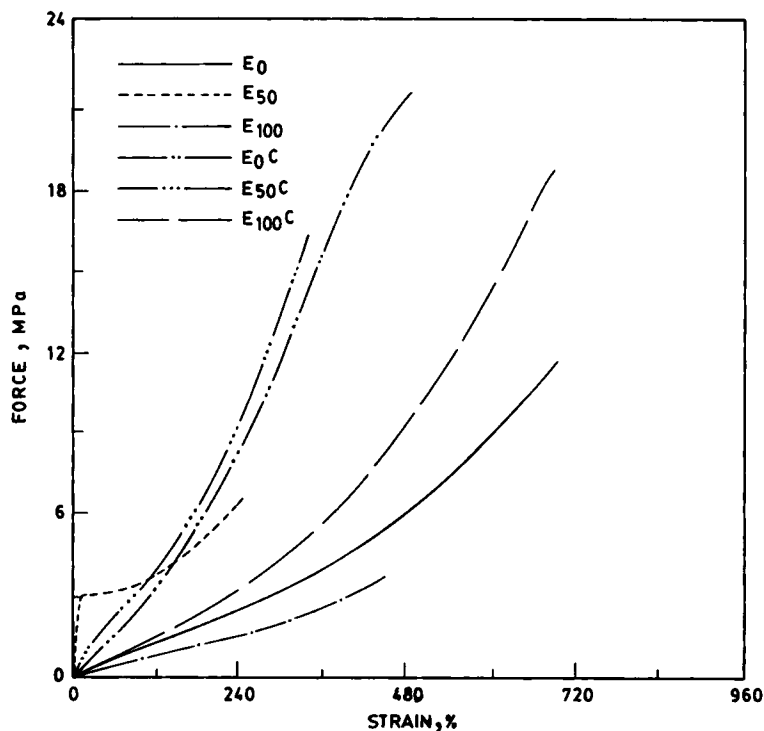

Figure 21   Stress–strain behavior of ENR-50, hypalon, their 1 : 1 blend (both gum and filled).
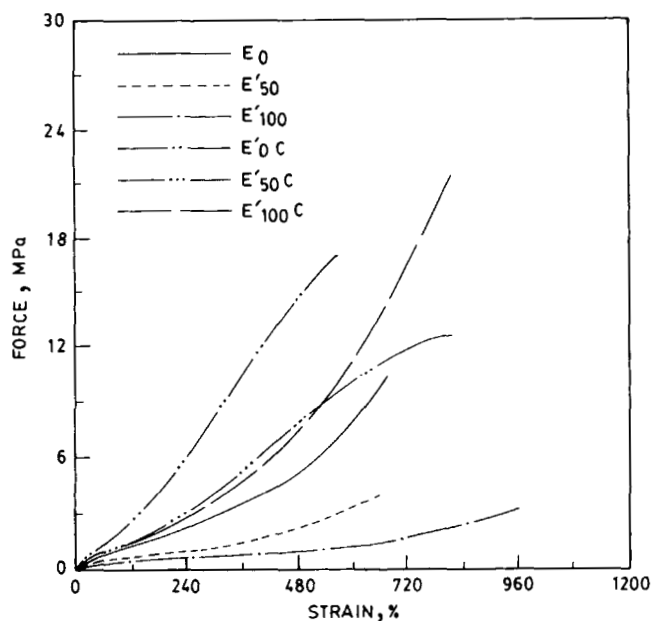
Figure 22   Stress–strain behavior of ENR-25, hypalon, their 1 : 1 blend (both gum and filled).

shown in Figure 17. The material seems to be chipped off by the abrasive due to low strength of the matrix and it shows low abrasion resistance. However, addition of carbon black improves the resistance to abrasion (Fig. 18).

In order to compare the self-vulcanization system with that of the conventional methods, ENR and hypalon were vulcanized individually. Processing characteristics of the single rubber mixes are shown in Tables IV and V. To eliminate the effect of crosslink density on physical properties, the single systems were vulcanized to the same crosslink density as that of the 50/50 blend of ENR/hypalon by keeping the rise in rheometric torque same. Low Mooney scorch time and high Mooney viscosity of the blend indicate that scorch safety of this self-vulcanized blend is less than that of the conventional single rubber mixes. The blends (both gum and filled) show marching increase in rheometric torque even up to 120 min at 150°C, indicating that it is thermally stable at that temperature. Gum ENR shows a broad plateau and hypalon a less prominent
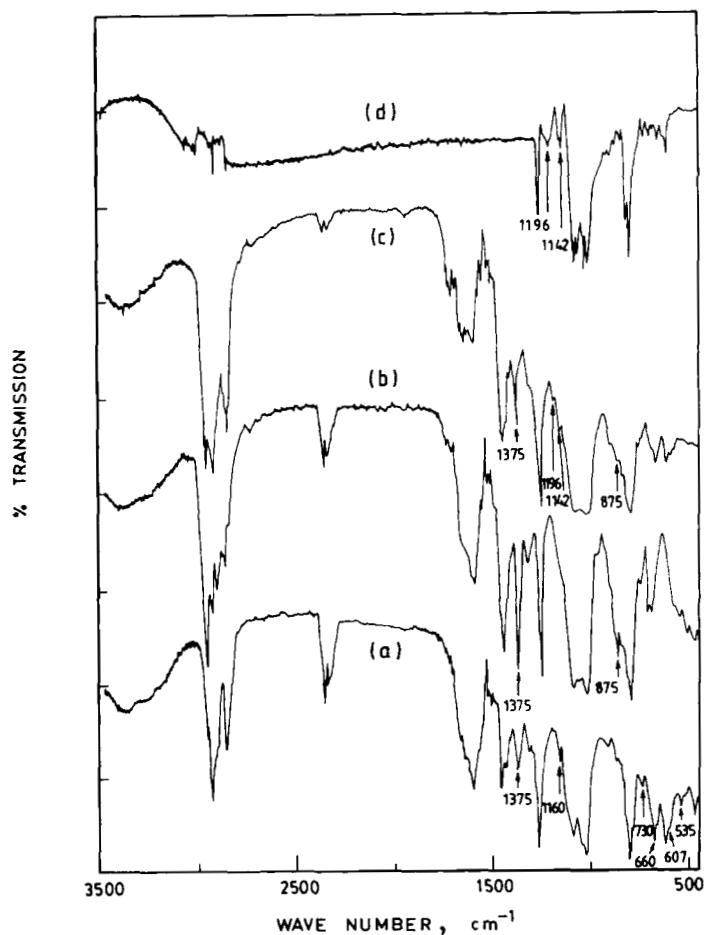

Figure 23   FTIR spectra of hypalon (a), ENR-50 (b), their 50/50 blend (c), and the difference spectrum (d).
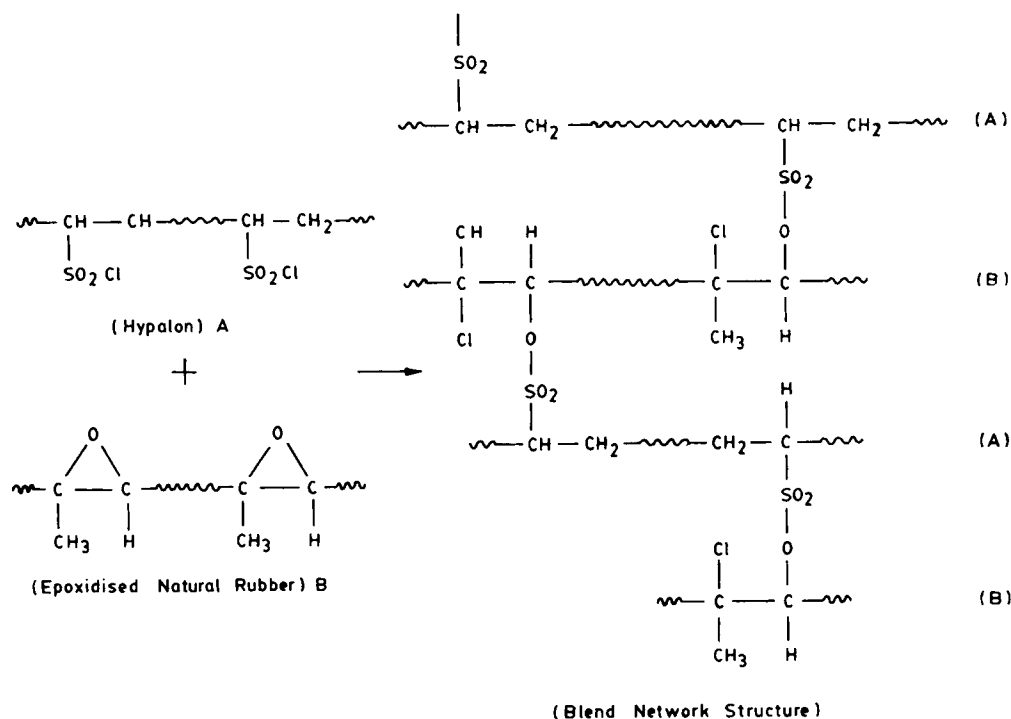
Figure 24 Proposed mechanism of reaction between ENR and hypalon.

marching modulus (Figs. 19 and 20). However, 20 parts of ISAF filled ENR-25 shows reversion after 20 min, whereas filled ENR-50 and hypalon show broad plateau.

Figures 21 and 22 show the stress–strain behavior of the control single rubbers and their 50/50 blends. ENR shows viscoelastic deformation of soft rubber whereas hypalon exhibits deformation of hard rubber. Addition of carbon black improves the modulus and tensile strength of the mixes, although the effect is more prominent in case of ENR.

It has been found that the properties of both ENR and hypalon are manifested in the self-vulcanized blend. For example, the blend has higher modulus, tensile strength, tear resistance, hardness, and abrasion resistance than the control ENR, but it has better permanent set properties than hypalon (Tables VIII and IX).

Figure 23 shows the FTIR spectra for hypalon (a), ENR-50 (b), the 50/50 blend (c), and their difference spectrum (d). The characteristics peaks of hypalon for SO_2 asymmetric and symmetric stretching vibration occur at 1375 and 1160 cm^{-1}, respectively, and that for C—Cl stretching vibration at 660, 607, and 535 cm^{-1}. The peaks for epoxide ring vibration in ENR occurs at 875 and 836 cm^{-1} and that for epoxide C—H vibration at 1375 cm^{-1}. It can be seen from Figure 23(c) that the intensity of the bands associated with ring vibration of ep-

oxide (875 and 836 cm^{-1}) and SO_2 asymmetric stretching vibration in hypalon (1375 cm^{-1}), which is also present in ENR for epoxide C—H vibration, are greatly reduced. The band for SO_2 symmetric stretching at 1160 cm^{-1} is found to be absent. Moreover, new bands at 1196 and 1142 cm^{-1}, which are due to SO_2 symmetric stretching vibration in sulfonates [$R(RO)SO_2$], are observed in the blend. This two bands are also detected when a difference spectrum [Fig. 23(d)] was computed. This observation supports the proposed mechanism of reaction between the SO_2Cl group of hypalon and the epoxy group of ENR forming sulfonate type of linkage. Similar mechanism has been reported for crosslinking of hypalon by epoxy resin.[17]

CONCLUSIONS

Blend of ENR and hypalon can be vulcanized during molding at high temperatures in the absence of any curatives. The extent of crosslinking reaction depends upon the level of epoxidation in ENR and blend composition. The self-vulcanized blend has better tensile and tear strength, hardness, and abrasion resistance than that of ENR and it has better permanent set as compared to hypalon. It can be reinforced by carbon black filler like conventional rubber systems.

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