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Effect of fillers and moulding conditions on properties of self-vulcanisable blends of epoxidised natural rubber and carboxylated nitrile rubber

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(Received 18 September 1989; revised version received and accepted 2 April 1990)

Abstract: A mill mixed blend of epoxidised natural rubber (ENR) and carboxylated nitrile rubber (XNBR) forms a self-vulcanisable rubber blend on moulding at high temperatures, when a crosslinking reaction occurs between the epoxy group of ENR and the carboxyl group of XNBR. Such a vulcanisate is reinforced by fillers like silica and carbon black.

1 Introduction

Mill mixed blends of functionally active rubbers can be vulcanised at high temperatures to form self vulcanisable rubber blends. De and co-workers have developed such blends based on epoxidised natural rubber, hypalon, carboxylated nitrile rubber, neoprene, halobutyl rubber and polyvinyl chloride.[1-5] It has been shown that a mill mixed blend of epoxidised natural rubber (ENR) and carboxylated nitrile rubber (XNBR) forms a self-vulcanisable and miscible rubber blend system during moulding at 140°C.[6-7] The crosslinking mechanism in such a self-vulcanisable rubber blend system is based on the reaction between the epoxy group of ENR and the carboxyl group of XNBR (Fig. 1). It has been reported earlier by Chakraborty and De[8] that carboxylated nitrile rubber can be vulcanised by epoxy resin.

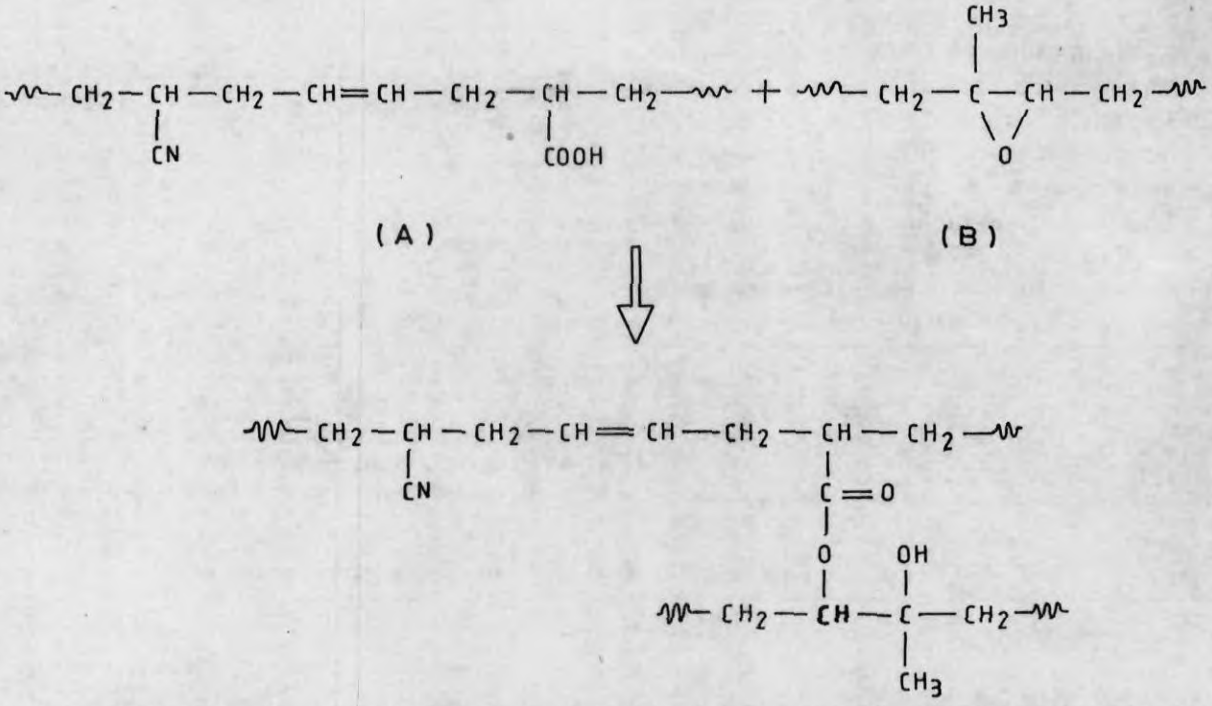

Fig. 1 The possible mechanism of crosslinking between carboxylated nitrile rubber (A) and epoxidised natural rubber (B).

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Plastics and Rubber Processing and Applications 0144-6045/90/$03.50 © 1990 The Plastics and Rubber Institute, England
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In the present paper we report the results of our studies on the effects of moulding temperature, moulding time and fillers on the properties of such self-vulcanisable rubber blends.

2 Experimental

Epoxidised natural rubber with 50 mol% epoxidation (ENR-50) was obtained from the Malaysian Rubber Producers Research Association, UK. Carboxylated nitrile rubber, containing a high level of carboxylated monomer and a medium high bound acrylonitrile level (Krynac 221) was obtained from Polysar Ltd, Canada. The silica filler used was Vulkasil S (precipitated silica) obtained from Bayer (India) Ltd, Thane.

Both ENR and XNBR were first individually masticated on a 0·356 m × 0·152 m (14 in × 6 in) two roll mixing mill for about 1 min each. The Mooney viscosities ($ML_{(1+4)}$ at 120°C) of ENR and XNBR before blending were 33 and 24 respectively. Masticated samples of the two rubbers were blended together in equal amounts on the mill for a further period of 6 min. Cold water was circulated through the rolls to keep the temperature low in order to avoid the rubber sticking on the rolls. The mill temperature for the initial mastication step was 25°C. The temperature rise during the mixing of gum rubber was only 2°C. The fillers were added after blending the two rubbers. The total mixing time for the filled blend was 10 min. The temperature rise during mixing in the case of filled blend was 7°C.

The formulation of the different blends is given in Tables 1 and 2. The formulation for the control mixes is given in Table 3.

In the case of blend, the increase in rheometric torque above the minimum torque was 30 units. The control mixes of ENR and XNBR were cured to the time when the rheometric torque rise was the same as that of the blend (that is 30 units). For ENR and XNBR these times were 18 and 12 min respectively, at 150°C. This was thought likely to eliminate the effect of curing time or crosslink density on the comparison of properties of blend and control vulcanisates.

Table 1. Formulation of XNBR–ENR blend mixes (in parts by weight)

Mix no.	Exb	Si10	Si20	Si30	Si40
ENR-50	50	50	50	50	50
XNBR (Krynac 221)	50	50	50	50	50
Silica (Vulkasil S)	—	10	20	30	40

Rheographs of the mixes were taken on Monsanto rheometer R-100 at 150, 160, 170 and 180°C. Scorch time and Mooney viscosity at 120°C were determined by using Mooney viscometer MK III (Negretti Automation Ltd) according to ISO 667. The properties determined as per standard test methods were tensile strength (ISO 37) using dumb bell specimens and an Instron 1195 universal testing machine; tear resistance (ASTM D624-84) using an unnicked 90° angle specimen (die C) and an Instron 1195 universal testing machine; hardness, shore A (ISO 7619), and resilience (BS: 903, part AB: 1963 method A) and a Dunlop tripsometer. Samples for compression set (ISO 815) were cylindrical discs 29 mm diameter and 13 mm thickness which were subjected to compressive deformation at constant strain for 22 h at 70°C. While determining heat build-up (ASTM D623-75), using a Goodrich flexometer, the samples were subjected to cyclic deformation for 25 min with a load of 10·89 kg (24 lb) and a stroke of 4·5 mm. Abrasion resistance (BS: 903, part [illegible] method A-1957) was determined by using a Du Pont abrader. In the Du Pont machine two test specimens were abraded simultaneously against an abrasive paper (silicon carbide paper with grain size 325). The specimens were held under a load of 3·62 kg and the abrasive paper rotated at a speed of 40 RPM. The samples were abraded for 10 min and then the volume lost (in m^3 from a specified test

Table 3. Formulation of control mixes (in parts by weight)

Mix no.	E	Ec	Es	X	Xc	Xs
XNBR (Krynac 221)	—	—	—	100	100	100
ENR-50	100	100	100	—	—	—
Na_2CO_3	0·25	0·25	0·25	—	—	—
ZnO	5	5	5	5	5	[illegible]
Stearic acid	2	2	2	2	2	[illegible]
ISAF black	—	20	—	—	20	—
Silica	—	—	20	—	—	20
Aromatic oil	—	2	2	—	—	—
Dioctyl phthalate	—	—	—	—	2	2
TMTD[a]	1·6	—	—	—	—	—
MBS[b]	2·4	1	1	1	1	1
Sulphur	0·3	2·8	2·8	2·4	2·4	2·4

[a] Tetramethylthiuram disulphide.
[b] *N*-Oxydiethylenebenzothiazole-2-sulphenamide.

Table 2. Formulation of XNBR–ENR blend mixes (in parts by weight)

Mix no.	IS5	IS10	IS15	IS20	IS30	IS40	SR5	SR10	SR15	SR20	SR30	SR40
ENR-50	50	50	50	50	50	50	50	50	50	50	50	50
XNBR (Krynac 221)	50	50	50	50	50	50	50	50	50	50	50	50
ISAF black	5	10	15	20	30	40	—	—	—	—	—	—
SRF black	—	—	—	—	—	—	5	10	15	20	30	40

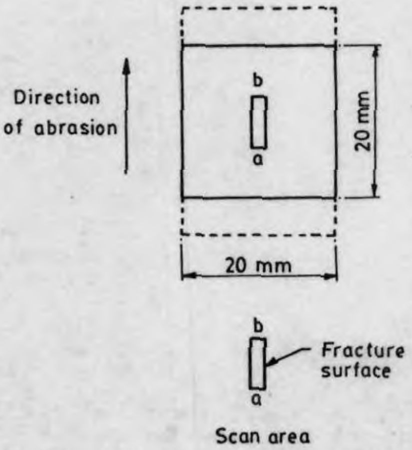


Fig. 2 Sample for abrasion tests showing fracture surface and scan area.

specimen for 1000 revolutions of the abrasive wheel) was calculated.

Scanning electron microscope (SEM) studies of abraded surfaces were done on a SEM, model CAN SCAN series 2DV. The shape, size and direction of abrasion of specimens are given in Fig. 2. After abrasion for 10 min the abraded surfaces were sputter coated with gold for SEM studies.

Table 4(a). Cure characteristics of different blends

Mix no.	Exb	Si10	Si20	Si30	Si40
Minimum Mooney viscosity at 120°C	35	43	59	66	100
Mooney scorch time at 120°C (min)	7·0	6·1	5·0	4·3	3·0
Monsanto rheometry					
Minimum torque at 150°C (dN m)	6	9	10	17	25
Maximum torque at 150°C (in 60 min) (dN m)	37	53	58	76	96
Minimum torque at 180°C (dN m)	6	8	9	12	20
laximum torque at 180°C (in 60 min) (dN m)	62	74	91	100	118

Volume fraction of the rubber in the swollen vulcanisate was calculated from equilibrium swelling data by the method reported by Ellis and Welding[9]

$$Vr=\frac{[D-FT/\rho_r]}{[(D-FT/\rho_r)+(Ao/\rho_s)]} \qquad (1)$$

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

3 Results and discussion

Minimum Mooney viscosities and Mooney scorch times for the gum and filled blends are given in Tables 4(a) and (b). It is evident that an increase of filler loading increases the minimum viscosity and decreases the scorch time. Also, the increase in Mooney viscosity and decrease in scorch time is most prominent in the case of silica-filled mixes and least prominent in the case of SRF black-filled mixes, while the ISAF black-filled mixes occupy an intermediate position. For example, at 40 PHR loading, Mooney viscosity at 120°C increases from 35 for the unfilled blend to 49 for SRF black, to 63 for ISAF black and to 100 for silica-filled blend. The higher Mooney viscosity of the silica-filled mix is probably due to strong interaction of the silica with the rubber during mixing. It is well known that ISAF black is more reinforcing than SRF black, hence the higher viscosity in the case of ISAF black-filled mix.[10]

Samples of neat ENR and neat XNBR were masticated for 8 min, which is also the blending time for the two rubbers, and the Mooney viscosity values, $ML_{(1+4)}$ at 120°C were determined. The values are as follows: ENR, 10; XNBR, 30, and blend, 35. It is evident that reaction between ENR

Table 4(b). Cure characteristics of different blends

Mix no.	IS5	IS10	IS15	IS20	IS30	IS40	SR5	SR10	SR15	SR20	SR30	SR40
Minimum Mooney viscosity at 120°C	35	39	43	43	58	63	36	39	39	39	41	49
Mooney scorch time at 120°C (min)	6·8	6·7	6·0	5·0	4·8	4·5	6·7	5·8	5·7	5·3	5·2	5·1
Monsanto rheometry												
Minimum torque at 150°C (dN m)	8	8	9	10	13	13	9	9	10	10	10	11
Maximum torque at 150°C (in 60 min) (dN m)	44	48	54	62	76	86	48	50	52	57	60	69
Minimum torque at 180°C (dN m)	8	8	8	8	10	10	7	7	8	8	8	8
Maximum torque at 180°C (in 60 min) (dN m)	75	87	92	92	113	130	69	75	84	88	106	109

Table 5. Cure characteristics of control mixes

Mix no.	E	Ec[a]	Es[b]	X	Xc[a]	Xs[b]
Minimum Mooney viscosity at 120°C	5	9	6	40	50	53
Mooney scorch time at 120°C (min)	10·0	6·5	20·0	3·8	2·0	2·5
Monsanto rheometry						
Minimum torque at 150°C (dN m)	2	3	2	11	12	12
Maximum torque at 150°C (dN m)	33	80	63	87	115	118

[a] 20 PHR ISAF black-filled.
[b] 20 PHR silica-filled.

and XNBR takes place to limited extent at 120°C during Mooney viscosity determination. The minimum Mooney viscosity and scorch time for the control mixes of ENR and XNBR are shown in Table 5. The mixes of XNBR are very scorchy compared to ENR mixes. It is reported that mixes of XNBR containing ZnO have a low scorch time and a high Mooney viscosity, where metal carboxylate crosslinks are formed.[11] In such mixes the low scorch time is due to the early onset of the reaction of the carboxyl group. The epoxy group of ENR permits effective crosslinking with chemicals like dibasic acids and polyamines.[12,13] Hence, the low scorch time of the blend mix of ENR and XNBR is due to the early onset of the reaction of the carboxyl group of XNBR with the epoxy group of ENR.

Rheographs of the gum blend (formulation Exb) at different temperatures 150, 160, 170 and 180°C are shown in Fig. 3. For comparison rheographs of one control XNBR mix and one control ENR mix (Table 3) were taken. It is evident that the rheometric torque of the blend progressively increases with moulding time and with moulding temperature. This shows that in the blend both XNBR and ENR crosslink each other during moulding and that both time and temperature cause progressive increase in crosslinking. At 150°C the self-vulcanisable blend registers marching rheometric torque like that of control XNBR compounds, while the ENR compounds show reversion. Crosslinking of ENR with dibasic acids has been reported to show a marching increase in modulus with cure time.[14] The XNBR system at 150°C shows much higher rheometric torque than the blend. Figure 4 shows the rheographs of the filled systems at 150°C. It is evident that addition of filler increases the rheometric torque as in the case of conventional rubber systems. The nature of rheographs with respect to moulding time and temperature is similar to that of gum blend. Increase of filler loading increases the rheometric torque.

It has been reported that the gum strength of dibasic acid cured ENR is greatly improved by the addition of reinforcing black.[14] In blend, the chemistry of vulcanisation and nature of crosslinks is different from conventionally cured ENR or XNBR.

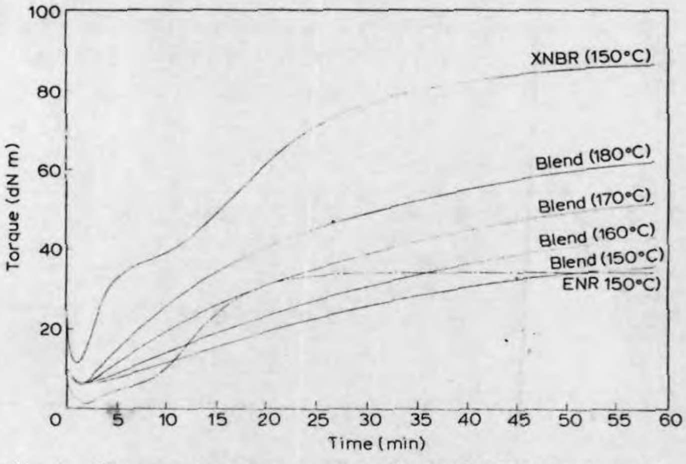


Fig. 3 Rheographs of a gum 1:1 ENR–XNBR blend at different temperatures and of control gum XNBR and ENR mixes at 150°C.

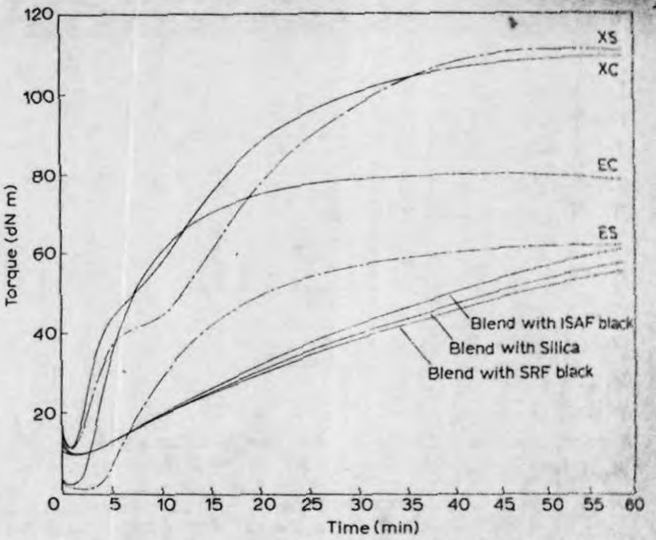


Fig. 4 Rheographs, at 150°C, of ENR, XNBR and 1:1 ENR–XNBR blend filled with 20 PHR loading of ISAF black, SRF black and silica filler.

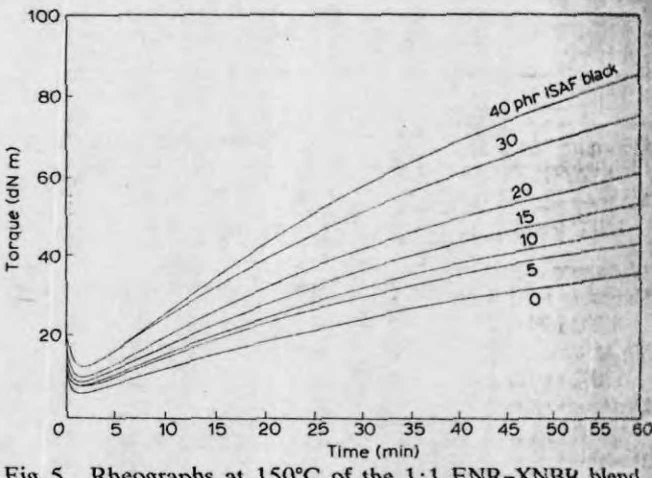
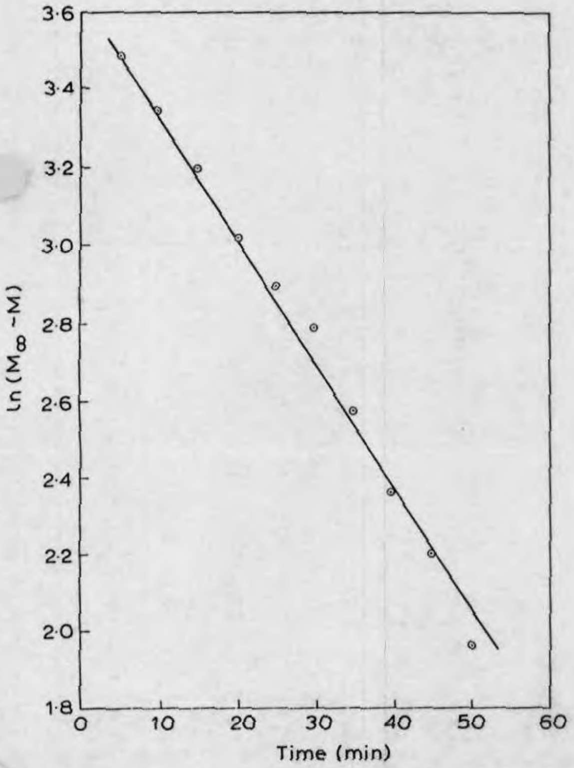


Fig. 5 Rheographs at 150°C of the 1:1 ENR–XNBR blend filled with different loadings of ISAF black filler.

In conventionally cured ENR crosslinking is by sulphur linkages[15] and in XNBR crosslinking is by sulphur linkages and metal carboxyl linkages.[11] In blends of ENR and XNBR the crosslinking reaction is by epoxy and carboxyl groups forming ester linkages which are distributed randomly in the matrix. Due to this difference in the mechanism of vulcanisation, the rheographs of blends show an absence of cure reversion, thermal stability of the crosslinked structure and a high cure rate.

Figure 5 shows the effect of ISAF black loading at 150°C. The cure characteristics of these mixes at temperatures 150 and 180°C are shown in Table 4. Enhancement of torque occurs in the following order: silica ≥ ISAF > SRF. As we shall see later, polymer–filler interaction also follows the same order.



Plot of $\ln(M_\alpha - M)$ versus time for the gum 1:1 ENR–XNBR blend at 150°C.

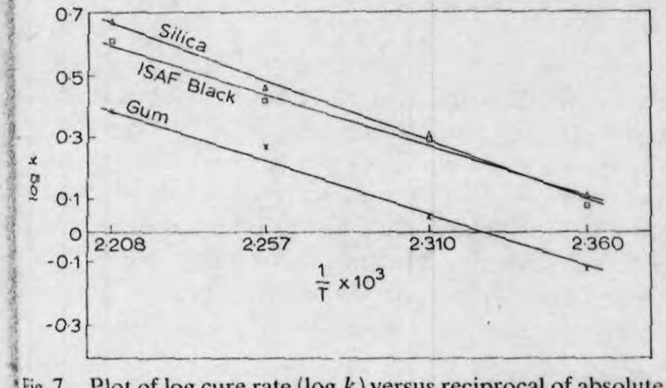


Fig. 7 Plot of log cure rate (log k) versus reciprocal of absolute temperature for the 1:1 ENR–XNBR blend and for the blend filled with 20 PHR ISAF black and silica filler.

The kinetics of a crosslinking reaction can be followed from the changes in rheometric maximum torque with time. For the first order reaction.[16,17]

$$\ln(M_\alpha - M) = -kt + \ln(M_\alpha - M_0) \qquad (2)$$

where M is the torque at time t, M_0 is the torque at zero time, and M_α is the maximum torque. For cure curves showing marching modulus, M_α was taken as the torque when the rise in torque is less than one unit in 5 min; at this stage it is assumed that the reaction has almost come to an end. From the linear plot

Table 6. Rate constant (*k*) of vulcanisation of the blend and control mixes at 150 and 180°C

	Rate constant, *k* (min^{-1} × 10^2)					
	E		X		Blend	
	150°C	180°C	150°C	180°C	150°C	180°C
Gum[a]	12·34	72·34	7·0	23·50	3·31	3·84
ISAF black-filled[a]	21·07	194·60	7·0	26·27	3·20	4·68
Silica-filled[a]	—	—	—	—	3·70	5·87

[a] Mix number Exb, IS20 and Si20 (Table 1).

Table 7. Activation energy for vulcanisation

	Activation energy, *E* (kJ/mol)		
	E	X	Blend
Gum[a]	77	34	65
ISAF black-filled[a]	86	43	65
Silica-filled[a]	—	—	70

[a] Mix number Exb, IS20 and Si20 (Table 1).

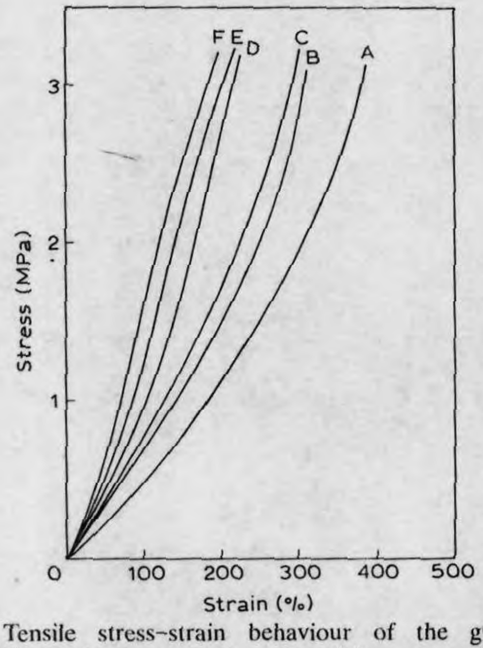


Fig. 8 Tensile stress–strain behaviour of the gum 1:1 ENR–XNBR blend moulded under different conditions of moulding time and temperature. (A) 150°C/30 min; (B) 150°C/45 min; (C) 150°C/60 min; (D) 160°C/60 min; (E) 170°C/60 min; (F) 180°C/60 min.

of $\ln(M_\alpha - M)$ versus time the rate constant of the first order crosslinking reaction can be determined. The activation energy for the initial vulcanisation reaction was calculated by using an Arrhenius equation. Figures 6 and 7 show typical plots for the calculation of rate constants and activation energies. Table 6 summarises the rate constants of blend and control mixes at two temperatures and Table 7 gives the values of the activation energy for vulcanisation. The activation energy for self vulcanisation is found to lie between 65 and 70 kJ/mol. This is of the same order of magnitude as reported by other workers for conventional rubbers.[18]

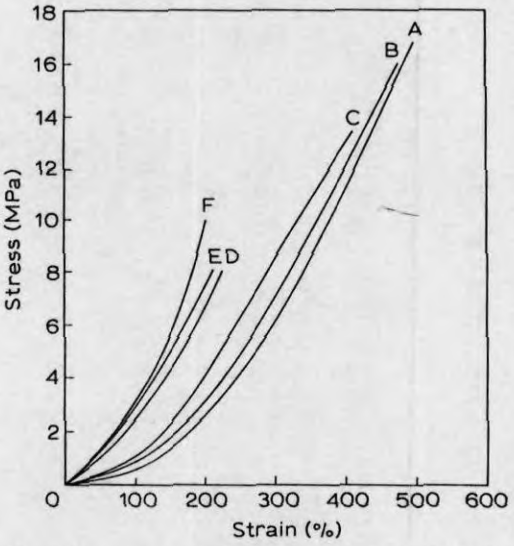


Fig. 9 Tensile stress–strain behaviour of the 1:1 ENR–XNBR blend filled with 20 PHR ISAF black and moulded under different conditions of time and temperature. (A) 150°C/30 min; (B) 150°C/45 min; (C) 150°C/60 min; (D) 160°C/60 min; (E) 170°C/60 min; (F) 180°C/60 min.

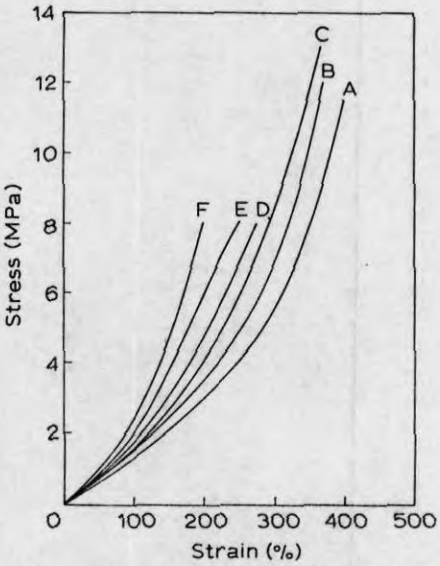


Fig. 10 Tensile stress–strain behaviour of the 1:1 ENR–XNBR blend filled with 20 PHR silica and moulded under different conditions of time and temperature. (A) 150°C/30 min; (B) 150°C/45 min; (C) 150°C/60 min; (D) 160°C/60 min; (E) 170°C/60 min; (F) 180°C/60 min.

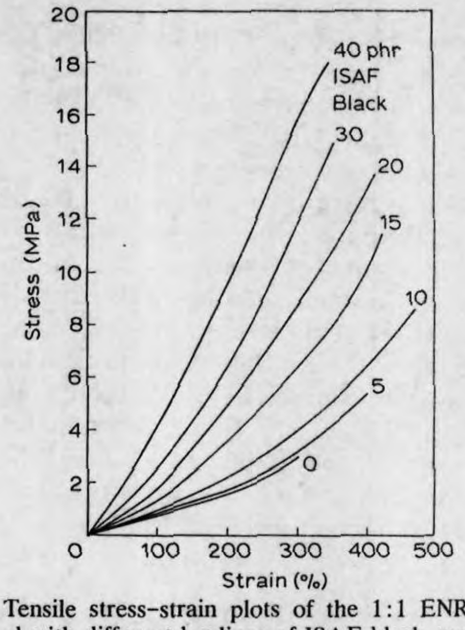


Fig. 11 Tensile stress–strain plots of the 1:1 ENR–XNBR blend filled with different loadings of ISAF black, moulded at 150°C for 60 min.

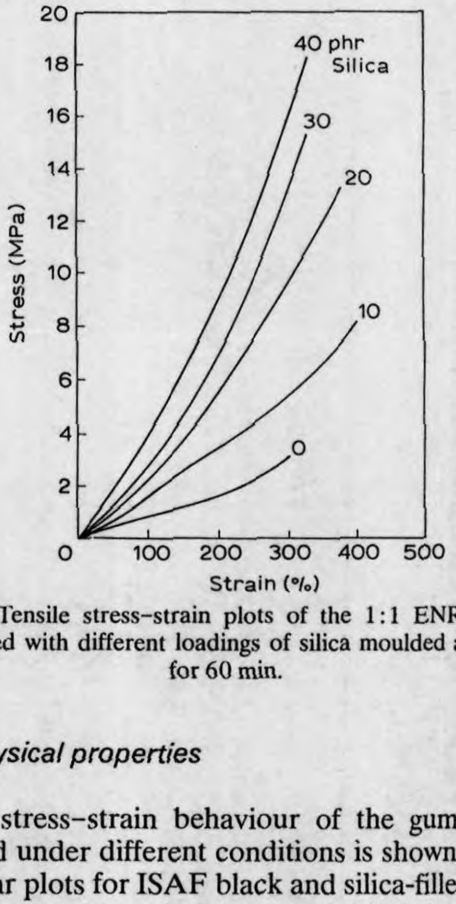


Fig. 12 Tensile stress–strain plots of the 1:1 ENR–XNBR blend filled with different loadings of silica moulded at 150°C for 60 min.

3.1 Physical properties

Tensile stress–strain behaviour of the gum blend moulded under different conditions is shown in Fig. 8. Similar plots for ISAF black and silica-filled compositions are shown in Figs 9 and 10. It is evident that both moulding time and temperature alter the stress–strain behaviour and the effect is prominent in filled systems. The effect of filler loading on stress–strain behaviour is shown in Figs 11–13. Energy at rupture increases with increasing filler loading and the trend continues up to the highest filler loading studied. The variation of rupture energy with filler loading is given in Fig. 14.

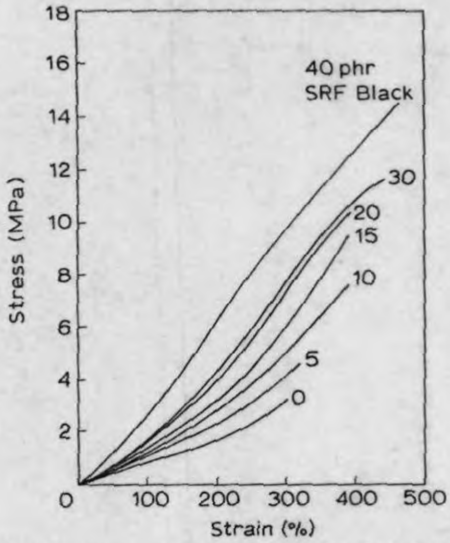


Fig. 13 Tensile stress–strain plots of the 1:1 ENR–XNBR blend filled with different loadings of SRF black, moulded at 150°C for 60 min.

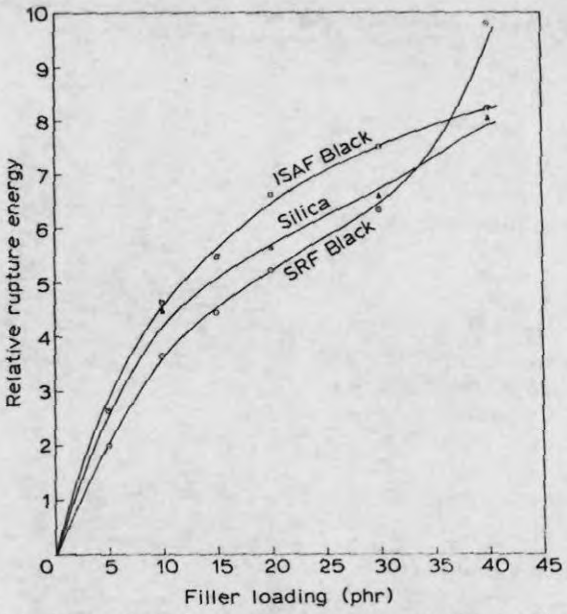


Fig. 14 Plots of relative rupture energy versus filler loading for ISAF black, SRF black and silica-filled 1:1 ENR–XNBR blend.

Table 8 summarises the results of the effect of moulding time at 150°C on some physical properties lik[illegible]odulus, tensile strength, elongation at break and tear resistance. It is evident that increasing moulding time at a constant temperature causes lowering of both tensile strength and tear resistance. However, as modulus increases, elongation at break decreases. Table 9 shows the results of the variation of moulding temperature at a constant moulding

Table 8. Effect of moulding time at 150°C on physical properties of the 1:1 XNBR–ENR blend

Time of moulding (min)	Gum			ISAF black[a]			Silica[a]		
	30	45	60	30	45	60	30	45	60
Modulus 100% (MPa)	0·5	0·8	0·8	0·6	0·7	1·1	1·3	1·4	1·5
Modulus 200% (MPa)	1·0	1·5	1·5	2·9	3·3	4·3	2·7	3·6	4·2
Modulus 300% (MPa)	2·0	2·8	3·2	6·2	7·0	8·9	5·3	7·1	9·2
Tensile strength (MPa)	3·0	3·1	3·2	17·0	16·0	13·5	12·0	12·0	13·0
Elongation at break (%)	340	310	300	500	470	410	400	370	370
Tear strength (kN/m)	17·0	16·0	12·6	53·0	47·0	38·0	33·0	29·0	29·0

[a] At 20 PHR loading.

Table 9. Effect of moulding temperature at constant moulding time (60 min) on physical properties of the 1:1 XNBR–ENR blend

	Gum		ISAF black[a]		Silica[a]	
	150°C	180°C	150°C	180°C	150°C	180°C
Modulus 300% (MPa)	3·2	—	8·9	—	9·2	—
Tensile strength (MPa)	3·2	3·2	13·5	10·0	13·0	8·0
Elongation at break (%)	300	200	410	200	370	200
Tear strength (kN/m)	12·6	11·8	38·0	27·0	29·0	23·0
Hardness, shore A	47	50	58	60	57	74
Resilience at 40°C (%)	69	74	61	67	64	70
Abrasion loss ($\times 10^{-6}$ m^3/1000 rev)	1·97	1·61	0·69	0·46	0·61	0·37
Compression set at 70°C for 22 h (%)	12	4	14	6	12	7
Heat build-up by Goodrich flexometer with a load of 10·89 kg and stroke of 4·5 mm						
ΔT^{b} (°C)	17	11	26	21	22	18
Dynamic set (%)	0·6	0·5	1·3	0·5	1·0	0·5
Vr	0·12	0·18	0·17	0·24	0·15	0·19

[a] At 20 PHR loading.
[b] Ambient temperature, 50°C.

Table 10. Physical properties of ISAF black filled 1 : 1 XNBR–ENR blend moulded at 150°C for 60 min

	Filler loading (parts per 100 of rubber)						
	0	5	10	15	20	30	40
Modulus 300% (MPa)	3·2	3·3	4·0	6·4	8·9	11·6	15·9
Tensile strength (MPa)	3·2	5·2	8·6	10·7	13·5	15·0	17·8
Elongation at break (%)	300	395	460	410	410	350	340
Tear strength (kN/m)	12·6	25·8	28·4	29·0	38·0	46·7	55·0
Hardness, shore A	47	49	53	55	58	67	76
Resilience at 40°C (%)	69	65	63	62	61	52	48
Abrasion loss ($\times 10^{-6}$ m^3/1000 rev)	1·97	1·54	0·80	0·72	0·69	0·46	0·30
Compression set at 70°C for 22 h (%)	12	13	14	14	14	15	17
Heat build-up by Goodrich flexometer with a load of 10·89 kg and stroke of 4·5 mm							
ΔT[a] (°C)	17	19	21	25	26	30	33
Dynamic set (%)	0·6	1·1	1·2	1·3	1·3	1·6	1·6
Vr	0·12	0·13	0·14	0·15	0·17	0·19	0·20

[a] Ambient temperature, 50°C.

Table 11. Physical properties of SRF black filled 1 : 1 XNBR–ENR blend moulded at 150°C for 60 min

	Filler loading (parts per 100 of rubber)						
	0	5	10	15	20	30	40
Modulus 300% (MPa)	3·2	3·7	4·9	6·3	7·3	7·6	9·8
Tensile strength (MPa)	3·2	5·2	7·6	9·2	10·5	11·5	14·5
Elongation at break (%)	300	310	385	390	390	440	460
Tear strength (kN/m)	12·6	26·0	28·0	29·5	30·9	36·0	47·0
Hardness, shore A	47	48	49	51	55	60	65
Resilience at 40°C (%)	69	69	68	68	66	59	57
Abrasion loss ($\times 10^{-6}$ m^3/1000 rev)	1·97	1·15	0·89	0·80	0·69	0·63	0·43
Compression set at 70°C for 22 h (%)	12	13	14	15	16	16	16
Heat build-up by Goodrich flexometer with a load of 10·89 kg and stroke of 4·5 mm							
ΔT[a] (°C)	17	18	19	20	21	23	30
Dynamic set (%)	0·6	0·6	0·6	0·7	0·7	0·7	1·0
Vr	0·12	0·13	0·13	0·14	0·15	0·16	0·18

[a] Ambient temperature, 50°C.

Table 12. Physical properties of silica-filled 1 : 1 XNBR–ENR blend moulded at 150°C for 60 min

	Filler loading (parts per 100 of rubber)				
	0	10	20	30	40
Modulus 300% (MPa)	3·2	5·0	9·2	13·4	16·0
Tensile strength (MPa)	3·2	8·0	13·0	15·3	18·0
Elongation at break (%)	300	400	370	330	330
Tear strength (kN/m)	12·6	26·0	29·0	40·0	49·7
Hardness, shore A	47	51	57	67	76
Resilience at 40°C (%)	69	64	64	60	55
Abrasion loss ($\times 10^{-6}$ m^3/1000 rev)	1·97	0·82	0·60	0·48	0·33
Compression set at 70°C for 22 h (%)	12	12	12	15	16
Heat build-up by Goodrich flexometer with a load of 10·89 kg and stroke of 4·5 mm					
ΔT[a] (°C)	17	19	22	24	30
Dynamic set (%)	0·6	1·0	1·0	1·1	1·4
Vr	0·12	0·13	0·15	0·19	0·20

[a] Ambient temperature, 50°C.

time on physical properties. It is observed that increase of moulding temperature from 150 to 180°C causes increasing hardness and resilience and decreasing abrasion loss, compression set, heat build-up and dynamic set. On the evidence of *Vr* values, these changes are ascribed to the formation of additional crosslinks at elevated temperatures.

Effects of filler loading on the physical properties are summarised in Tables 10–12. As expected, the following properties show a gradual increase with increasing filler loading: modulus, tensile strength, tear strength, abrasion resistance hardness, heat build-up and dynamic set. Resilience decreases gradually and compression set increases with filler loading.

In order to understand abrasion mechanism we have analysed SEM fractographs of the abraded surfaces. In abrasion, mechanical, chemical and thermal processes are involved.[19] Reznikoiskii and Broskii have described different types of wear in elastomers.[20] High abrasion resistance is observed in vulcanisates with high hardness, modulus, tensile strength, tear strength, resistance to thermo-oxidative degradation and crack growth resistance under dynamic conditions.[21] Such elastomeric vulcanisates show ridge formation during abrasion.[22,23] Figures 15 and 16 show the failure surfaces of E and EIS 20 (formulations in Table 3). In ENR the abrasion resistance is very poor and the material seems to be chipped by the abrasive. This is due to low matrix strength as seen from tensile properties and hardness. The cut growth resistance is also poor as rubber is removed in lumps by the abrasive. When filler is added, the abrasion resistance is improved due to high matrix strength. There is ridge formation in XNBR vulcanisates and blends as seen from Figs 17–21. Gum XNBR and ISAF black-filled XNBR show high abrasion resistance and follow frictional type wear (Figs 17 and 18).

The gum blend shows abrasive type wear (Fig. 19). Here the abrasion resistance is better than pure ENR due to a higher matrix strength. At low ISAF black loading (20 PHR) the blend shows the abrasive type wear, and at higher ISAF black loading (40 PHR) the mechanism of wear changes from an abrasive to a frictional type (Figs 20 and 21). It has been reported that low ridge height and close spacing of ridges, as noted in the present case of black-filled blend and XNBR, are indicative of high abrasion resistance.[24]

Although the self-vulcanisable rubber blend system is similar to conventional rubber vulcanisates

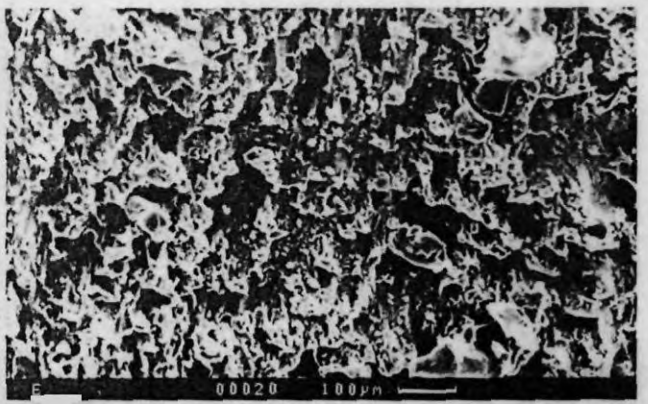


Fig. SEM micrograph of the gum ENR vulcanisate showing a coarse abrasion pattern.

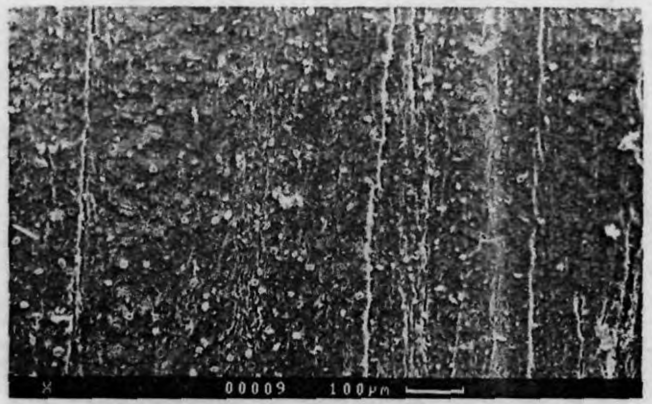
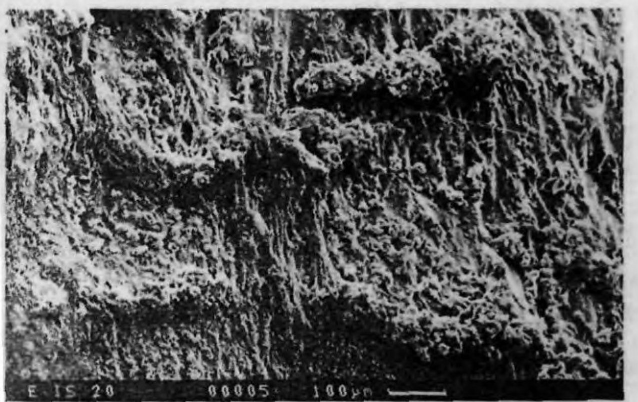


Fig. 17 Abraded surface of the gum XNBR vulcanisate showing clear surface.



ig. 16 SEM micrograph of a filled (20 PHR ISAF black) ENR vulcanisate showing material removal.

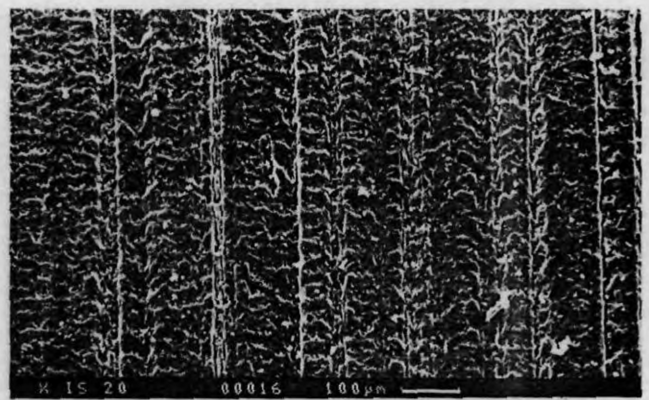


Fig. 18 Abraded surface of the 20 PHR ISAF black-filled XNR vulcanisate showing fine and closely spaced ridges.

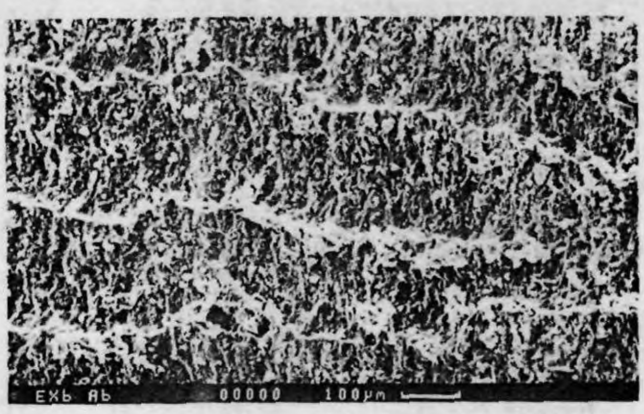


Fig. 19 Abraded surface of the 1:1 ENR–XNBR blend showing abrasive type of wear.

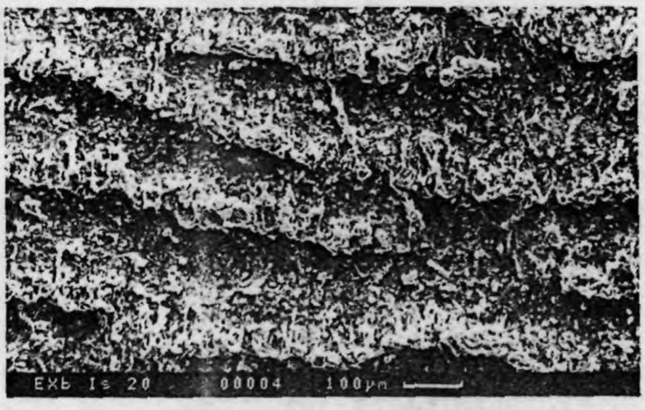


Fig. 20 Abraded surface of the 1:1 ENR–XNBR blend filled with 20 PHR ISAF black showing ridges which are not closely spaced.

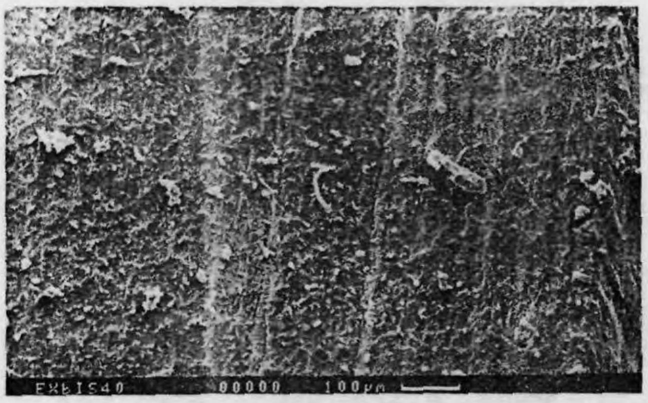


Fig. 21 Abraded surface of the 1:1 ENR–XNBR blend filled with 40 PHR ISAF black showing closely packed fine ridges.

as regards the influence of filler, silica reinforcement in such blend occurs even in the absence of a coupling agent and the extent of silica reinforcement is similar to the ISAF black reinforcement. The degree of reinforcement occurs in the following order: SRF < ISAF = silica. Reinforcement can be related with the polymer–filler interaction. An indication of polymer–filler interaction can be obtained from the Kraus plot.[25] It has been shown elsewhere that both ENR and XNBR vulcanisates can be reinforced by silica in the absence of coupling agent.[26,27]

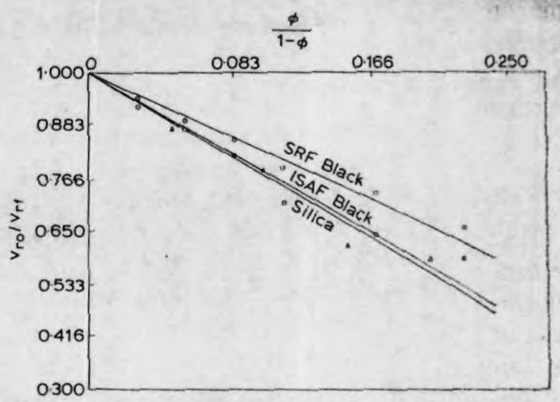


Fig. 22 Kraus plots for ISAF black, SRF black and silica-filled 1:1 ENR–XNBR blend.

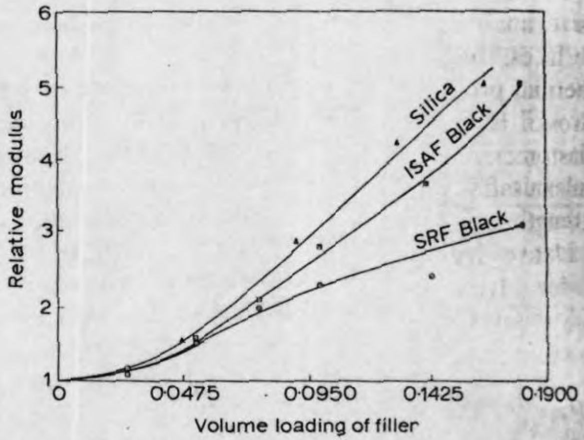


Fig. 23 Variation of relative modulus with volume fraction of filler for a 1:1 ENR–XNBR blend filled with silica, ISAF black and SRF black and moulded at 150°C for 60 min.

The plot of $V_{ro}/\nu V_{rf}$ against $\phi/(1-\phi)$ is shown in Fig. 22. The slope of the plot is maximum for the silica-filled blend and minimum for the SRF black-filled blend. The slope of the ISAF black-filled blend is close to the silica-filled blend. Accordingly, we observe that polymer–filler interaction increases in the order: SRF < ISAF ≤ silica. It has been noted earlier in this paper that reinforcement in physical properties also follows the same order. The plot of relative modulus versus volume fraction of filler shown in Fig. 23. The increase in relative modulus with filler loading also follows the same trend. Accordingly, we conclude that filler reinforcement of the self-vulcanisable rubber blend system is similar to the filler reinforcement of conventional rubber vulcanisates.

For comparison, we have included in our studies two control systems based on XNBR alone and ENR alone. These mixes were cured to a rheometric torque rise similar to the corresponding blend mixes.

Table 13 shows properties of the XNBR–ENR blend and the control vulcanisates, for both gum and filled systems. The blend shows higher resilience and lower compression set than the corresponding control ENR and XNBR vulcanisates. The difference in

Table 13. Physical properties of the XNBR–ENR blend with control XNBR and ENR systems

Mix no.	E	X	Exb	Ec	Xc	IS20	Es	Xs	Si20
Modulus 300% (MPa)	1·2	3·9	3·2	9·0	15·5	8·9	6·9	13·0	9·2
Tensile strength (MPa)	4·2	18·7	3·2	23·0	24·0	13·5	18·0	25·1	13·0
Elongation at break (%)	650	470	300	595	380	410	500	400	370
Tear strength (kN/m)	18·4	34·2	12·6	49·0	69·7	38·0	39·0	60·7	29·0
Hardness, shore A	30	69	47	61	83	58	53	81	57
Resilience at 40°C (%)	26	62	69	49	54	61	49	52	64
Abrasion loss ($\times 10^{-6}$ m^3/1000 rev)	8·40	0·02	1·97	0·42	0·05	0·70	2·00	0·06	0·60
Compression set at 70°C for 22 h (%)	16	70	12	35	53	14	23	45	12
Heat build-up by Goodrich flexometer with a load of 10·89 kg and stroke of 4·5 mm									
ΔT^a (°C)	20	—	17	16	58	26	18	41	22
Dynamic set (%)	1·6	—	0·6	7·3	4·2	1·3	8·0	13·0	1·0
Vr	0·09	0·05	0·12	0·12	0·10	0·17	0·12	0·16	0·15

[a] Ambient temperature, 50°C.

the property is ascribed to the type of vulcanisate network structure.

Conclusions

ENR ad XNBR forms a self-vulcanisable rubber blend. This blend shows marching modulus with increasing moulding time and temperature. The poor gum strength of the blend is improved by addition of reinforcing fillers. The processability and curing characteristics of the blend depend on the type and amount of filler used. The blend vulcanisates show low compression set and high resilience when compared with conventionally cured XNBR and ENR. Silica reinforcement in self-vulcanisable blend occurs in the absence of any coupling agent.

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