AGEING AND STRESS RELAXATION OF SELF-VULCANISED EPOXIDISED NATURAL RUBBER-CARBOXYLATED NITRILE RUBBER BLEND.

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ABSTRACT

Stress relaxation of self-vulcanised epoxidised natural rubber (ENR)-carboxylated nitrile rubber (XNBR) blend under different ageing conditions like aqueous acid, aqueous alkali and hot air have been studied. The unaged self-vulcanised blend like conventional rubber vulcanisates showed two relaxations in the time range of 10^4 sec. Compared to XNBR vulcanisates the blend showed a much lower decay of stress with time. The self-vulcanised blend showed better ageing resistance towards acid, alkali and hot air as reflected from tensile properties and stress relaxation studies. This could be attributed to the various structural changes taking place under the different ageing conditions.

INTRODUCTION

Self-vulcanisable rubber blends is a novel class of rubber blends which crosslink by themselves without the aid of vulcanising agents when heated at high temperatures. Examples are blends based on ENR[1], XNBR[2], polychloroprene[3] (CR) and hypalon[4]. The characterisation[5], polymer filler interaction[6] and rheological aspects[7] of self-vulcanisable binary ENR-XNBR blend has been documented. In this communication we report the results of our studies on ageing and stress relaxation characteristics, of this blend.

EXPERIMENTAL

Formulation of the mixes are shown in Table 1. Both ENR and XNBR were first individually masticated on a laboratory size two roll mixing mill for about 1 min each. The masticated samples of the two rubbers were blended together in equal amounts on the mill for a further period of six minutes. The filler ISAF black was added after blending the two rubbers.

Table 1: Formulation of the mixes.(phr)

	E	Ec	X	Xc	Exb	Exbis 20
ENR-50	100	100	--	--	50	50
XNBR (Krynac 221)	--	--	100	100	50	50
Na_2CO_3	0.25	0.25	--	--	--	--
ZnO	5	5	5	5	--	--
Stearic acid	2	2	2	2	--	--
ISAF black	--	20	--	20	--	20
Aromatic oil	--	2	--	--	--	--
Dioctyl phthalate	--	--	--	2	--	--
TMTD[a]	1.6	--	--	--	--	--
MBS[b]	2.4	1	1	1	--	--
Sulphur	0.3	2.8	2.4	2.4	--	--

A tetramethyl thiuram disulphide.
b N-oxydiethylene benzothiazole-2-sulphenamide.

Stress relaxation and ageing studies were carried out using dumpbell shaped test specimens.The samples were subjected to the following three different ageing conditions.

1. Air ageing at 70°C for twelve days, in an air oven.
2. Aqueous acid ageing, 25% HCl, at 70°C for seven days.
3. Aqueous alkali ageing, 25% NaOH at 70°C for seven days.

RESULTS AND DISCUSSION

Plots of σ/σ_0 (σ_0 is obtained from the maximum stress at t = 0, when the desired strain is reached, σ is the stress at subsequent times) versus log (time) for the unaged vulcanisates are shown in Figure 1 .Stress relaxation parameters[8] obtained are shown in Table 2.

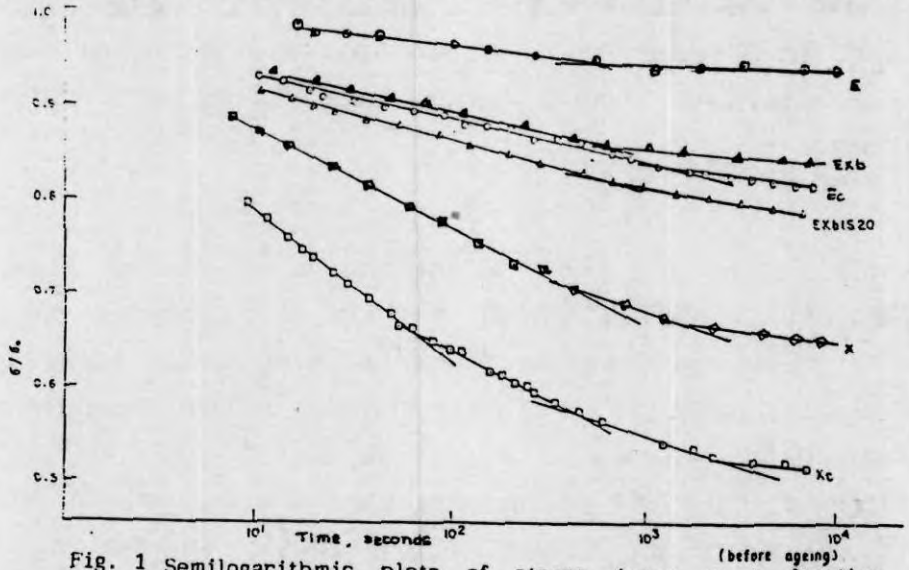

Fig. 1 Semilogarithmic plots of stress decay as a function of time for the gum and filled vulcanisates

The stress relaxation behaviour of all unaged vulcanisates could be fitted on two straight lines as observed earlier for unfilled rubber vulcanisates[9-12]. The existance of a second line with slope lower than the first line indicated two relaxation mechanisms operating in the time range studied. The first relaxation could be due to small segments or domains of molecular chains[8] and the second due to rearrangement of molecular chains or aggregates[13]. It was observed that time after which the slope changed was high for ENR and low for XNBR, while the blend had a value which was in between the two single rubbers. The comparatively high stress relaxation could be due to the high hysterises caused by ionic crosslinks in XNBR[14,15]

Table 2: Ageing and stress relaxation data of the test vulcanisates.

Sample	Conditions	Modulus, MPa 300%	Tensile strength, MPa	Elongation at break, %	Slope of log log plots of stress relaxation data
E	Original	1.50	3.3	590	0.012
	Air 70°C/12 d*	--	1.4	250	0.010
	Acid 70°C/7 d	--	6.4	15	--
	Alkali 70°C/7 d	1.40	2.1	440	0.016
Ec	Original	6.2	25.5	790	0.020
	Air 70°C/12 d	--	9.0	280	0.031
	Acid 70°C/7 d	--	0.5	7	--
	Alkali 70°C/7 d	7.5	17.5	580	0.025
X	Original	5.5	15.1	600	0.041
	Air 70°C/12 d	6.3	11.0	430	0.047
	Acid 70°C/7 d	--	4.0	192	--
	Alkali 70°C/7 d	6.3	7.2	335	0.033
Xc	Original	10.4	23.5	570	0.059
	Air 70°C/12 d	16.0	23.3	405	0.066
	Acid 70°C/7 d	--	8.0	173	--
	Alkali 70°C/7 d	--	13.4	268	0.051
Exb	Original	2.3	2.7	350	0.017
	Air 70°C/12 d	--	2.6	190	0.012
	Acid 70°C/7 d	--	3.0	181	0.024
	Alkali 70°C/7 d	--	2.3	155	0.016
Exbis 20	Original	7.8	9.8	360	0.024
	Air 70°C/2 d	--	11.0	280	0.024
	Acid 70°C/7 d	--	6.6	145	0.035
	Alkali 70°C/7 d	9.6	9.9	307	0.028

* days.

AIR AGEING

Stress relaxation data of air aged samples at 70°C for 12 days is shown in Table 2 The blend showed better retention of tensile properties than the control ENR vulcanisates.

ACID AGEING

The blend vulcanisates showed a much less stress decay than the control mixes in the time range studied (Table 2). The ENR vulcanisates after acid ageing became very brittle and could not be stretched to 150% strain. The XNBR vulcanisates also showed poor stress relaxation properties. This behaviour could be correlated with structural changes occuring during ageing as reflected from tensile properties.

ALKALI AGEING

The changes in both tensile properties and stress relaxation is less prominent after alkali ageing. The stress relxation of all mixes show close similarity to unaged vulcanisates (Table 2). However, alkali ageing increases the decay of stress, as observed from Table 2. This behaviour correlates well with the aged tensile properties.

CONCLUSION

The blend vulcanisates showed two relaxations like the conventional rubber vulcanisates, in the time range studied.

Ageing studies under different ageing conditions like hot air, acid and alkali showed that the blend had better resistance to ageing than control single rubber vulcanisates. This could be attributed to the structural changes occuring during the different ageing conditions.

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