Self-vulcanizable ternary rubber blend based on epoxidized natural rubber, carboxylated nitrile rubber and polychloroprene rubber: 2. Effect of blend ratio and fillers on properties

R. Alex, P. P. De and S. K. De

Rubber Technology Centre, Indian Institute of Technology, Kharagpur, 721302, India (Received 9 May 1990; revised 30 August 1990; accepted 30 August 1990)

Mill-mixed blends of epoxidized natural rubber (ENR), carboxylated nitrile rubber (XNBR) and neoprene form a self-vulcanizable ternary blend system which can be reinforced by fillers such as carbon black and silica. The effect of fillers on processing characteristics and physical properties of self-vulcanizable blends is similar to that of conventional rubbers. The properties depend on blend ratio and type of filler. The blend in the gum state shows poor failure properties like gum ENR, but shows high resilience and low compression set. Abrasion loss and heat build-up properties of the blend are nearer to those of gum neoprene vulcanizate. The filled blends show lower heat build-up due to non-uniform distribution of fillers in the miscible ternary blend. Mooney viscosity and Mooney scorch time of the blend are found to be intermediate between the control mixes of ENR and XNBR, but the Monsanto rheometric torque values are closer to ENR.

(Keywords: ternary blends; miscibility; mechanical properties)

INTRODUCTION

In earlier papers^{1,2} it has been reported that a mill-mixed blend of epoxidized natural rubber (ENR), polychloroprene rubber (neoprene) and carboxylated nitrile rubber (XNBR), forms a self-vulcanizable ternary rubber blend system upon moulding at 150°C. It has been observed that miscibility of such systems depends on blend composition and incorporation of filler². The processing and physical properties of these blends have not been studied with respect to blend ratio variation and effect of filler. In this paper we report the results of studies on dependence of vulcanization characteristics and physical properties of the ternary blends on blend composition and fillers such as ISAF black, silica and SRF black. Similar studies have previously been made on the self-vulcanizable binary blend system of ENR/XNBR³.

EXPERIMENTAL

Epoxidized natural rubber (ENR) with 50mo1% epoxidation was obtained from Malaysian Rubber Producers' Research Association, UK. Carboxylated nitrile rubber containing a high level of carboxylated monomer and a medium level of bound acrylonitrile (Krynac 221) was obtained from Polysar Ltd, Canada. Neoprene AD was obtained from DuPont Ltd, UK. Vulcasil S (precipitated silica) was obtained from Bayer (India) Ltd, Bombay.

ENR and XNBR were separately masticated for \sim 1 min and neoprene for \sim 2 min on a 14 \times 6 in. two roll mixing mill. Masticated samples of neoprene and XNBR were blended for \sim 2 min and after addition of ENR were blended for a further 2min. The mill

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temperature for the initial mastication was 25°C. The temperature rise during the mixing of gum rubbers was only 2°C. The fillers were added after blending **the** rubbers. The total mixing time for the filled blends was \sim 12 min. The temperature rise during mixing in the case of filled blends was 7°C. The rolls were kept cool by **the** circulation of cold water.

Formulations of different blends are shown in *Tables* I and 2. Formulations of the control mixes are given in *Table 3.* In the case of the blend the increase in rheometric torque above the minimum torque was 26 units. The control mixes of ENR and XNBR were cured until the rise in rheometric torque was the same as that of the blend, i.e. 26 units. The cure times thus obtained were 30 min, 9 min and 60 min for ENR, XNBR and neoprene respectively.

Rheographs of the mixes were taken on a Monsanto Rheometer R-100 at 150, 160, 170 and 180°C. Scorch time and minimum Mooney viscosity at 120°C were determined using Mooney viscometer MK III (Negretti Automation Ltd), according to ISO 667. The properties determined by standard test methods were: tensile strength, (ISO 37) using dumbbell specimens by Instron 1195 Universal Testing Machine; tear resistance (ASTM D624-84) using an unnicked 90° angle specimen die C by Instron 1195 Universal Testing Machine; hardness, shore A (ISO 7619); and resilience (BS 903: part A8: method A: 1963) by Dunlop tripsometer. Samples for compression set (ISO 815) were cylindrical discs 29 mm diameter and 13 mm thickness, subjected to compressive deformation at constant strain for 22 h at 70°C. While determining heat build-up (ASTM D623-75) by Goodrich flexometer the samples were subjected to cyclic deformation for 25 min at an ambient temperature of

Table 1 Formulation of blends

phr, parts per hundred neoprene/XNBR blend

Table 2 Formulations of filled ternary blends (in phr)

a ISAF, Intermediate Super Abrasion Furnace

b SRF, Semi Reinforcing Furnace

cPrecipitated silica, Vulcasil S obtained from Bayer (India) Ltd, Bombay

 $TMTO = Tetramethylthiuram disulphide$

NBS = N **-oxydiethylene benzothiazole-2-sulphenamide**

50°C with a load of 24lb (\approx 10.8 kg) and stroke of 4.5 mm. Abrasion resistance (BS 903: part A9: method A: 1957) was determined using a DuPont abrader. Samples were abraded with the abrasive paper rotating at a speed of 40 rev min⁻¹. The volume (in cm³) lost from a specified test specimen for 1000 revolutions of the abrasive wheel was then calculated.

Scanning electron microscope (SEM) studies of the abraded surfaces were made on a scanning electron microscope model Camscan series 2 DV. The size, shape and direction of abrasion of specimens are shown in *Figure 1.* The abraded surfaces were sputter-coated with gold for SEM studies.

Volume fraction (V_r) of the rubber in the swollen vulcanizate was calculated from equilibrium swelling data by the method reported by Ellis and Welding⁴:

$$
V_{\rm r} = \frac{(D - FT)/\rho_{\rm r}}{\left[(D - FT)/\rho_{\rm r} \right] + (A_0/\rho_{\rm s})}
$$
(1)

where T is the weight of the specimen, D is the swollen weight, F is the weight fraction of insoluble components and A_0 is the weight of absorbed solvent corrected for swelling increment. ρ_r and ρ_s are the densities of the rubber and solvent respectively. Chloroform was used as the solvent in this study.

RESULTS AND DISCUSSION

Effect of blend ratio variation

Cure characteristics. Results of cure characteristics are

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shown in *Table 4.* For a constant neoprene/XNBR ratio, minimum Mooney viscosity and scorch time at 120°C show progressive change with ENR content. As the ENR content increases, the minimum Mooney viscosity decreases and scorch time increases. As the XNBR in the neoprene/XNBR ratio increases, the scorch time is greatly reduced and minimum Mooney viscosity is increased. For instance at a neoprene/XNBR ratio of 75/25 when ENR at 25 parts per hundred parts neoprene/XNBR blend (phr) is added, minimum Mooney viscosity is 33 and scorch time is 10.8 min. However, at a neoprene/XNBR ratio of 25/75 with 25 phr ENR, minimum Mooney viscosity is 45 and scorch time is 5.1 min. In the ternary blend it is believed that the carboxyl group of XNBR and the epoxy group of ENR react to form ester linkages^{5,6} and the epoxy group of ENR and allylic chlorine of neoprene react to form ether linkages⁷. Furthermore $-COOH$ group of XNBR has been reported to interact with allylic chlorine of neoprene in order to form a self-vulcanizable rubber blend⁸. Hence the low scorch time in ternary blends containing high XNBR is due to early onset of chemical reactions involving -COOH group, epoxy group and allylic chlorine.

Monsanto rheographs of the different blends at 150°C are shown in *Figure 2.* All the blends show increasing

Figure 1 Abrasion sample showing direction of abrasion and scan area

rheometric torque with time. The dependence of minimum rheometric torque on the blend ratio follows the same pattern as the changes in minimum Mooney viscosity. At a fixed neoprene/XNBR ratio, increase in ENR content lowers the Mooney viscosity. The extent of crosslinking, as reflected from the rheometric torque, depends on the composition of the blend. Maximum rheometric torque was observed in blend G which contains neoprene/XNBR/ENR in the ratio 1/3/3. Blend G has been found to be completely miscible and a homogeneous matrix is formed at the composition at which maximum interaction between the constituents takes place.

Physical properties. The physical properties of different gum blends are shown in *Table* 5. Tensile stress *versus* strain curves are shown in *Figure 3*. High tensile strength is observed in blends containing a high proportion of neoprene. The systems which contain a high proportion of neoprene are immiscible at the segmental level, but are mechanically compatible. Immiscible systems which are mechanically compatible are reported to have good physical properties 9'1°. For neoprene/XNBR blends at 75/25 and 50/50 ratios, increased incorporation of ENR causes a decrease in modulus, tensile strength, tear strength, hardness and resilience and an increase in compression set and abrasion loss. Values of V_r were found to decrease with increased ENR content. Since V_r

Figure 2 Monsanto rheographs of different gum ternary blends at 150°C. (a) Blends: $-\cdots$, I; $-\cdots$, H; $-\cdots$, L; $-\cdots$, G; 150°C. (a) Blends: $-\cdots$, I; $-\cdots$, H; $-\cdots$, L; $-\cdots$, G; , M. (b) Blends: $---, D;$ $---, E;$ $---, F.$ (c) Blends: **, A;** ----, **B**; ---, **K**; ----, **C**; ----, **J**. Compositions of blends as given in *Table 1*

Property	Blend (neoprene/XNBR/ENR ratio)								
	A (3/1/3)	B (3/1/2)	C (3/1/1)	D (2/2/3)	E (2/2/2)	F (2/2/1)	G (1/3/3)	H (1/3/2)	(1/3/1)
Modulus 300% (MPa)	2.5	2.8	6.4	3.5	3.5	6.1		5.0	4.8
Tensile strength (MPa)	9.3	8.6	15.5	5.0	5.8	9.7	4.7	5.3	5.4
Elongation at break $(\%)$	550	510	440	380	370	370	270	310	330
Tear strength $(kN m^{-1})$	33	29	39	23	26	27	18	18	23
Hardness (Shore A)	60	65	75	55	58	65	49	52	55
Resilience at 40° C (%)	57	62	62	63	65	67	68	66	65
Compression set, 22 h at 70° C (%)	57	30	30	30	27	19	11	13	13
Abrasion loss cm^3 10 ⁻³ rev)	2.0	2.0	1.8	2.0	2.0	0.7	1.8	1.2	0.5
Heat build-up by Goodrich flexometer with a load of 24 lb and stroke of 4.5 mm, ΔT (°C)	\boldsymbol{a}	\boldsymbol{a}	\pmb{a}	\boldsymbol{a}	\boldsymbol{a}	\pmb{a}	38 ^b	\boldsymbol{a}	\boldsymbol{a}
$V_{\rm r}$	0.06	0.07	0.10	0.10	0.11	0.11	0.13	0.13	0.11

Table 5 Physical properties of gum ternary blends moulded for 60 min at 150°C

^aSample blown out before 20 min bValue after 20 min

Figure 3 Tensile stress *versus* strain curves of ternary gum vulcanizates. Blend compositions as given in *Table 1*

can be considered as proportional to crosslink density, the gradual changes in properties could be understood on the basis of degree of crosslinking. However, in neoprene/XNBR blend at 25/75 ratio, increased incorporation of ENR causes an increase in V_r and accordingly the changes in properties with blend ratio variation follow a different pattern. In general, the changes in properties with blend ratio variation are less remarkable in this series.

Effect of fillers

Cure characteristics. Minimum Mooney viscosities and Mooney scorch times for the filled blend⁹ are given in *Table* 6. As expected, an increase of filler loading increases the minimum viscosity and decreases the scorch time. The increase in Mooney viscosity is very high in the case of silica-filled mixes and low in the case of SRF black-filled mixes. For example, at a loading of 40 parts filler per hundred parts rubber (phr), Mooney viscosity at 120°C increases from 30 for the unfilled blend to 49 for SRF black-filled mix, to 71 for ISAF black-filled mix and to 98 for silica-filled mix. The higher Mooney viscosity of silica-filled mix is probably due to the strong interaction of silica with rubber during mixing at higher $temperatures^{11,12}$. The low scorch times of the blends show that the crosslinking reaction starts even at a processing temperature of 120°C.

Rheographs of the gum blend at different temperatures and of control ENR, XNBR and neoprene mixes at 150°C are shown in *Figure 4.* The gum blend shows increasing rheometric torque with time and temperature of moulding. *Figure 5* shows rheographs of ISAF black-filled systems. It is evident that, as in the case of conventional rubbers, ISAF black reinforces the ternary blend. The nature of rheographs with respect to time and temperature is similar to that of gum blend. Increase of filler loading increases the rheometric torque *(Figure 6).*

It has been reported that both neoprene and XNBR can be cured by epoxy resins^{12,13}. Furthermore neoprene and XNBR interact to form ester linkages. In the ternary blend of neoprene/ENR/XNBR it is likely that ether linkages and ester linkages will be distributed randomly in the matrix. Conventionally cured vulcanizates with sulphur linkages show a tendency for reversion. On the other hand, due to the difference in the type of crosslinks, the ternary blend shows an absence of cure reversion and a higher degree of crosslinking at higher temperatures.

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Figure 4 Rheographs of gum blend G at different temperatures and of control ENR, XNBR and neoprene mixes at 150°C

Figure 5 Rheographs at 150°C of ISAF black-filled systems of: ., single ENR; blend G $-$, XNBR; $-\cdots$, neoprene; $-\cdots$, ternary

Physical properties. The tensile stress *versus* strain behaviour of the filled mixes is shown in *Figure 7.* The effect of filler loading on the physical properties is summarized in *Table 7.* As expected, the following

Figure 6 Rheographs at 150°C of ternary blend G filled with different loadings of ISAF black

properties show gradual increase with increase in filler loading: modulus, tensile strength, tear strength, abrasion resistance and hardness. Resilience decreases with filler loading. It is interesting to note that heat build-up is considerably reduced for filled mixes at higher loading of filler. There is believed to be an unequal distribution of reinforcing filler in the ternary blend and this has been reported to result in low hysteresis^{14,15}.

Polymer-filler interaction was studied by swelling of the blend vulcanizates in chloroform. *Figure 8* shows the variation of $V_{\text{ro}}/V_{\text{rf}}$ against $\phi/(1-\phi)$ according to the Kraus plot¹⁶:

$$
V_{\rm ro}/V_{\rm rf} = 1 - m\phi/(1 - \phi) \tag{2}
$$

where ϕ is the volume concentration of filler in the filled vulcanizate, V_{ro} is the volume fraction of rubber phase in swollen gel of gum rubber vulcanizate and V_{rf} is the volume fraction of rubber phase in swollen gel of filled rubber vulcanizate, assuming that filler does not swell. Both V_{ro} and V_{rf} are determined by equation (1). *m* is a constant characteristic of the filler-rubber matrix.

It is evident that the linear relation according to the Kraus plot is not obeyed in this system. This deviation from linearity may be due to two reasons. Firstly, fillers

Figure 7 Tensile stress *versus* strain curves of the miscible ternary blend G filled with different loadings of (a) silica, (b) SRF black and (c) ISAF black

Figure 8 Kraus plots for ternary blend G filled with ISAF black (0) , SRF black (\square) and silica (\triangle)

have been reported to influence the miscibility of the ternary blend². Affinities of the three rubbers for the fillers are not the same and therefore fillers will tend to redistribute when mixed into a blend. This can result in

an accumulation of fillers at the interface 17 and consequently some portion of fillers will not be available in the rubber matrix for resisting solvent penetration. This would cause a lower V_{rf} than expected, resulting in an increase in the ratio of $V_{\text{ro}}/V_{\text{rf}}$. Secondly, fillers themselves take part in crosslinking reactions which may result in an increase in crosslink density of the network. Accordingly the actual V_{ro} value in the filled blend will be higher than the measured V_{ro} value of the gum blend. As a result the ratio of $V_{\text{ro}}/V_{\text{rf}}$ will be higher than the value obtained if there were no increase in crosslink density due to filler incorporation.

The abrasion characteristics of the blends have been studied by SEM. Ridge formation in elastomers has been reported previously $18-20$. It has been shown that close spacing of ridges results in high abrasion resistance²¹. Abrasion resistance depends mainly on the strength of the matrix. The gum ternary blend has poor matrix strength which is greatly improved by the addition of reinforcing fillers, The SEM fractographs of the abraded surfaces of the ternary blend, showing the effect of reinforcing filler on abrasion resistance, are shown in *Figures 9-11.* The abraded surface of the gum mix *(Figure* 9) shows horizontal ridges which are deformed and widely spaced showing poor abrasion resistance. With incorporation of 20 phr ISAF black the abraded surface shows a tendency to form vertical ridges *(Figure 10).* When the ISAF black loading is raised to 40 phr closely spaced vertical ridges *(Figure 11)* are formed showing that the

Figure 9 SEM fractograph of abraded surface of blend G

Figure 10 SEM fractograph of the abraded surface of blend G filled with 20 phr ISAF black

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Table 7 Physical properties of the filled ternary blend G moulded for 60 min at 150°C

°Reading after 20 min

^bReading after 15 min

cSample blown out before 15 min

^dSample blown out

Figure 11 SEM fractograph of abraded surface of blend G filled with 40 phr ISAF black

abrasion resistance is improved. Vertical ridge formation suggests frictional type wear²².

Physical properties of the ternary blend and of control ENR, XNBR and neoprene mixes are shown in *Table 8.* The observations can be summarized as follows.

- 1. As expected gum neoprene shows high strength, due to strain crystallization. Addition of reinforcing ISAF black does not change the physical properties significantly. However, addition of 20 phr ISAF black reduces the elongation at break and causes reduction in the abrasion loss and compression set.
- 2. Gum XNBR shows good matrix strength, excellent abrasion resistance but high compression set due to ionic crosslinks. Incorporation of 20 phr ISAF black causes improvement in most of the physical properties. However, abrasion resistance remains unaffected by the presence of ISAF black.

^aReading after 20 min

^bSample could not be tested

cSample blown out

aValues from *Table 4*

- 3. Gum ENR shows poor matrix strength which, however, is reinforced on addition of 20 phr ISAF black filler.
- 4. The self-vulcanizable ternary blend in the gum state registers poor failure properties, as does gum ENR, but it shows high resilience and low compression set. Abrasion loss and heat build-up properties of the blend are nearer to those of gum neoprene matrix. Addition of 20 phr reinforcing black causes improvement in all physical properties.

Cure characteristics of the ternary blend G and of control ENR, XNBR and neoprene mixes are shown in *Table 9.* Mooney viscosity and scorch time of the blend were found to be intermediate between the two control mixes of ENR and XNBR, but the Monsanto rheometric torque values are close to ENR.

CONCLUSIONS

Mill-mixed blend of ENR, XNBR and neoprene forms **^a**self-vulcanizable ternary blend system. Processing characteristics, crosslink density and physical properties of this blend depend upon blend ratio. Incorporation of reinforcing fillers, such as ISAF black, precipitated silica and SRF black, causes changes in processing behaviour and physical properties which are similar to conventional rubber mixes.

Silica forms strong polymer-filler bonds during mixing in the ternary blend system as is evident from processing characteristics.

Due to non-uniform distribution of fillers in the blend components Goodrich heat build-up of filled composites is less than the unfilled blend.

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