

Self-crosslinkable ternary blend of chlorosulphonated polyethylene, epoxidized natural rubber and carboxylated nitrile rubber

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Incorporation of carboxylated nitrile rubber (XNBR) to an immiscible and self-crosslinkable blend of chlorosulphonated polyethylene (CSM) and epoxidized natural rubber (ENR) can result in a miscible ternary rubber blend composition, which is also self-crosslinkable. It was observed by dynamic mechanical analysis that the miscibility in the ternary blend system (containing CSM and ENR in the ratio of 1:1) can be achieved when the XNBR level is higher than 50% of the total composition. XNBR is found to play a dual role: reactive compatibilization as well as plasticization of the system. The self-crosslinking characteristics of the blends were studied by Monsanto rheometry, differential thermal analysis and swelling experiments. Stress-strain properties were also investigated to confirm the homogeneity of the blends.

(Keywords: chlorosulphonated polyethylene; epoxidized natural rubber; carboxylated nitrile rubber; self-crosslinkable rubber blend; miscible rubber blend)

INTRODUCTION

In recent years, De and co-workers¹⁻⁷ have found that blends of elastomers with reactive functional groups are capable of undergoing crosslinking reactions in the absence of any vulcanizing agent. It has been reported by the same authors that self-crosslinked blends based on epoxidized natural rubber (ENR)-carboxylated nitrile rubber (XNBR) and chlorosulphonated polyethylene (CSM)-carboxylated nitrile rubber are miscible in all compositions¹⁻³. In fact, the miscibility of the self-crosslinked blends of CSM and ENR depends on the epoxy content of ENR and the blend ratio. For example, 50:50 and 75:25 blends of CSM and ENR with 50% epoxidation are immiscible, whereas the 25:75 blend is miscible.

There has recently been growing interest in the multi-component mixtures of polymers. Several reports on ternary blends of polymeric materials have been published⁸⁻²⁴, but most of them have focused on homogenizing two immiscible polymers by adding a third component that is miscible with both. In the present report, our aim is to assess the compatibilizing action of XNBR on the immiscible self-vulcanizable 50:50 binary blend of CSM and ENR-50. As a compatibilizer, the behaviour of XNBR is unique in the sense that it interacts chemically with the other two components, whereas conventional compatibilizing agents usually interact by physical means.

EXPERIMENTAL

Epoxidized natural rubber with 50 mol% epoxidation (ENR-50) was supplied by the Malaysian Rubber Producers' Research Association, UK. Carboxylated

nitrile rubber containing high levels of carboxylated monomer (7 mol%) and a medium high acrylonitrile level (Krynac-221) was obtained from Polysar Ltd, Canada. Chlorosulphonated polyethylene containing 35% chlorine and 1% sulphur (Hypalon-40, DuPont Ltd, USA) was used for the present study.

Formulations of the blends are given in *Table 1*. ENR and XNBR were separately masticated for about 1 min each and CSM was milled for 4 min on a 14 × 6 inch two-roll mixing mill, keeping a tight nip gap. CSM and ENR were blended first and XNBR was added and blended further. The total blending time was 5 min.

Rheographs were taken at 160°C using a Monsanto rheometer R-100. The vulcanization of the blends was carried out at 160°C for 60 min under 10 MPa pressure using a small laboratory press. The moulded samples were taken out after cooling to room temperature under pressure by passing cold water through the platens of the press.

Dynamic mechanical studies were carried out between -100 and 50°C at 3.5 Hz, under tension mode, using a

Table 1 Formulations of blends and their T_g values

Blend designation	Blend ratio (parts by wt)		T_g^a (°C)
	CSM	ENR-50:XNBR	
X_0	50/50/0		-9.1, 24.7
X_{15}	43.5/43.5/13		-12.3, 20.7
X_{20}	41.6/41.6/16.8		-13.2, 18.6
X_{25}	40/40/20		-13.2, 16.8
X_{50}	33.3/33.3/33.3		-12.8, 14.6
X_{75}	28.6/28.6/42.8		-13.2, 10.6
X_{100}	25/25/50		^b , 2.7
X_{125}	22.2/22.2/55.6		^b , 0.8

^aObtained from $\tan \delta$ maxima by dynamic mechanical analysis

^bNot detectable

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dynamic viscoelastometer (Rheovibron model DDV-III-EP, Orientec Corporation, Japan). The strain amplitude used was 0.0025 cm and the heating rate was 2°C min⁻¹.

Differential thermal analysis (d.t.a.) was performed on a Shimadzu DT-40 differential thermal analyser. A heating rate of 20°C min⁻¹ was employed using a sample size of 10 mg.

Tensile tests were performed using a Zwick model 1445 universal testing machine according to ASTM D 412-87. At least five specimens of each sample were used to obtain an average value.

The volume fraction of rubber, V_r , in the vulcanized blends swollen to equilibrium was estimated by the method reported by Ellis and Welding²⁵.

$$V_r = \frac{D\rho_r^{-1}}{D\rho_r^{-1} + A_0\rho_s^{-1}} \quad (1)$$

where D is the deswollen weight of the test piece, A_0 is the equilibrium weight of the liquid imbibed (corrected for swelling increment) and ρ_r and ρ_s are the densities of rubber and solvent, respectively. For the present study, chloroform was used as the solvent for swelling experiments.

RESULTS AND DISCUSSION

Monsanto rheographs of representative blends are presented in *Figure 1*. An increase in rheometric torque with time reflects progressive crosslinking of the system. It is obvious that cure reversion is absent at 160°C even up to 60 min and the crosslinked network is thermally stable at this temperature. It is noteworthy that the rise in rheometric torque (i.e. the difference between the torque at 60 min and the minimum torque value) increases with the progressive increase in XNBR content of the ternary blend up to a certain XNBR level, beyond which the rise in torque decreases. Besides, the blends containing low levels of XNBR show a steady increase in rheometric torque, indicating that the crosslinking reaction is not complete in 60 min. On the contrary, the blends containing higher levels of XNBR (>30%) exhibit completion of crosslinking within 60 min. From these observations, it is apparent that up to a certain limit, the increase in XNBR content increases the availability of carboxyl groups, resulting in an enhancement of the rate and the extent of crosslinking. In the present ternary blend system, self-crosslinking is believed to be due to the reactions between CSM-ENR, CSM-XNBR and ENR-XNBR and all these reactions

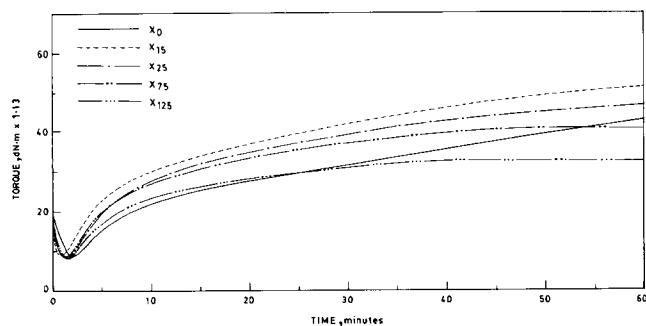


Figure 1 Rheographs of CSM-ENR (50:50) binary (blend X_0) and CSM-ENR-XNBR ternary blends

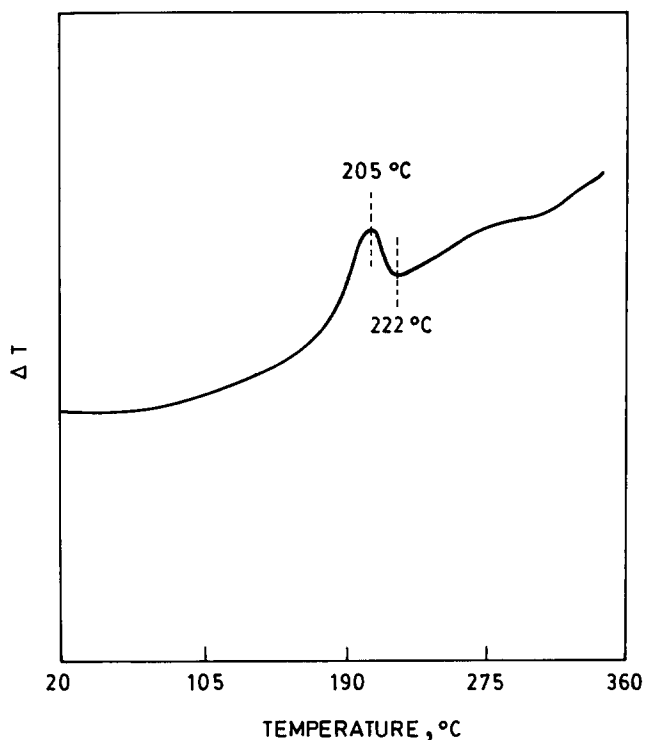


Figure 2 D.t.a. thermogram of a ternary blend of CSM-ENR-XNBR (33.3:33.3:33.3)

take place simultaneously. In the blend compositions where the level of XNBR is less than that of the other two components, it is likely that all three reactions occur side by side to a considerable extent. In the blends containing higher concentrations of XNBR, the relative amounts of CSM and ENR become less, and CSM-XNBR and ENR-XNBR reactions presumably dominate over the reaction between CSM and ENR. These competitive reactions among the components of the blend are expected to explain some features of the rheographs.

Figure 2 shows a typical d.t.a. curve of a representative blend (blend X_{50}). The thermogram shows an exothermic peak at 205°C. This provides further evidence for self-crosslinking of the blend in the absence of vulcanizing agent. Furthermore, CSM, ENR and XNBR are soluble in chloroform, whereas the moulded blends are insoluble indicating that a crosslinked network structure is formed during moulding.

Dynamic mechanical properties

The temperature dependence of the loss tangents ($\tan \delta$) and storage moduli of the blends are shown in *Figures 3* and *4*. It must be noted that the binary CSM-ENR (50:50) blend has two loss peaks indicating the heterogeneity of the blend. The peak positions (-9°C and 25°C) do not correspond either to CSM (-5°C) or to ENR (-9.5°C). This fact strongly suggests that some structural changes take place or some new species are formed during the crosslinking reactions of the blend. *Figures 3* and *4* also illustrate the effect of a progressive increase in XNBR level in ternary blends (in all these ternary blend compositions, the ratio of CSM and ENR is kept constant at 1:1). It is noteworthy that the positions of both relaxation peaks characteristic of the 50:50 CSM-ENR blend are affected as the amount of XNBR

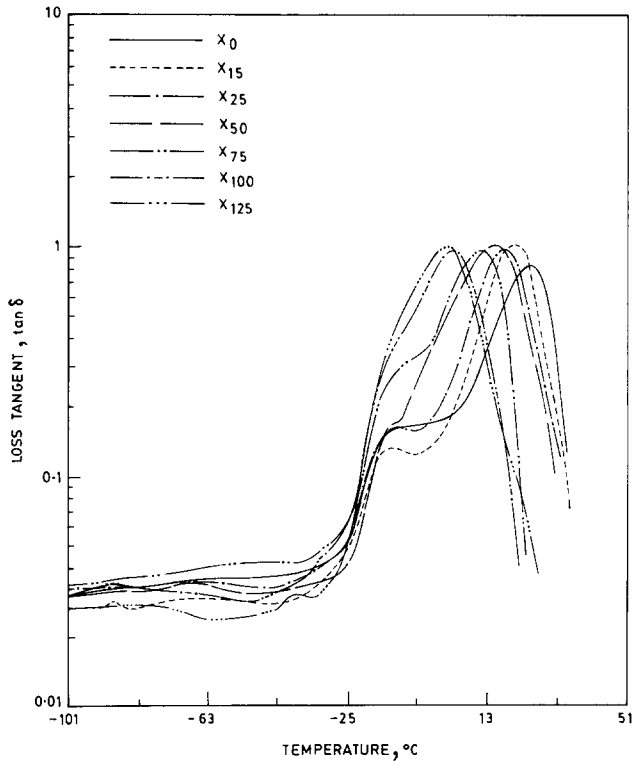


Figure 3 Temperature dependence of loss tangent ($\tan \delta$) for CSM-ENR (50:50) binary (blend X_0) and CSM-ENR-XNBR ternary blends

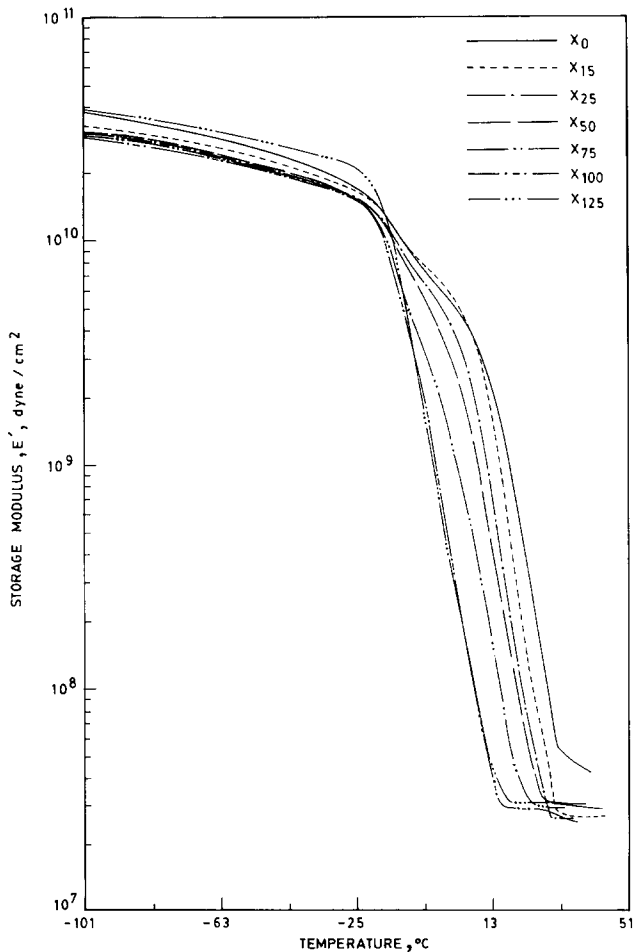


Figure 4 Temperature dependence of storage modulus for CSM-ENR binary (blend X_0) and CSM-ENR-XNBR ternary blend system

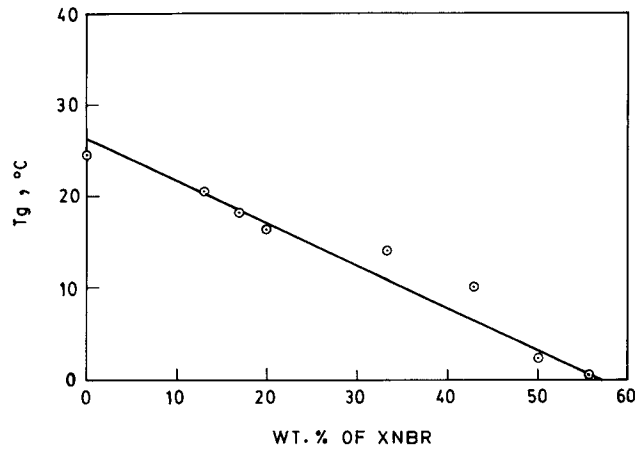


Figure 5 Composition dependence of glass transition temperature (from high temperature relaxation maximum) for CSM-ENR-XNBR ternary blend system

in the ternary blend system goes up. Table 1 and Figure 5 summarize the effect of variation of XNBR levels on T_g s of the blends (T_g corresponding to the α relaxation peak of XNBR is -11.4°C). As shown in Figure 3, the $\tan \delta$ peaks move towards lower temperatures as the proportion of XNBR in the blend is increased. The shift is rather striking in the case of the high temperature relaxation peak. On the other hand, the low temperature relaxation peak is initially shifted toward slightly lower temperature; after that it remains almost constant and finally vanishes as the level of XNBR in the blend is increased. At XNBR levels higher than 50%, the blends show single composition dependent glass transition temperatures, indicating that homogeneity of the blends is achieved. Figure 5 shows the concentration dependence of the location of the high temperature relaxation peak. The temperature corresponding to the relaxation maximum changes linearly with the concentration of XNBR in the blend. This is considered to result from reactive compatibilization as well as plasticization of the binary CSM-ENR blend by XNBR. The plasticization by XNBR is also corroborated by the storage modulus versus temperature plots (see Figure 4). The dynamic modulus values monotonically decrease with increasing levels of XNBR in the blend. Static modulus values (Figure 6) also show a similar trend. The plasticizing effect of XNBR may be explained on the basis of the availability of the reactive functional groups present in the three individual components of the blends. Both CSM and ENR contain high concentrations of reactive functional groups, but in XNBR the amount of reactive groups is lower (only 7%). So the crosslink densities of CSM-XNBR and ENR-XNBR blends are expected to be lower than that of the CSM-ENR blend and this is also substantiated by swelling studies.

V_r values of ENR-XNBR (50:50) and CSM-XNBR (50:50) in chloroform are 0.15 and 0.09, respectively, whereas that of CSM-ENR (50:50) is 0.176. The percentage volume swelling and volume fraction of rubber swollen in chloroform of a few representative blends are given in Table 2. Both the parameters increase initially with the increase in XNBR content up to a critical concentration, thereafter an opposite trend is observed, that is, decrease in V_r value with increase in XNBR level.

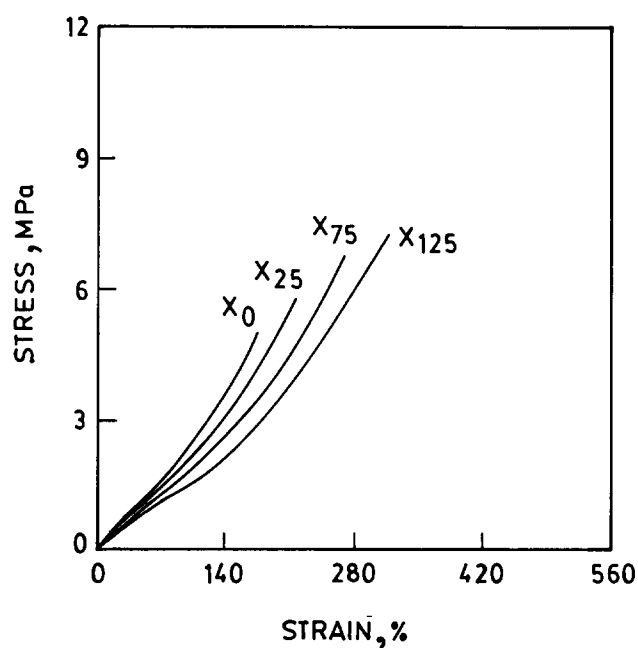


Figure 6 Stress-strain properties of CSM-ENR (50:50) binary (X_0) and CSM-ENR-XNBR ternary blends

Table 2 The percentage volume swelling and volume fraction of rubber in swollen vulcanizate (V_r) at 35°C using chloroform as the solvent

Blend designation	Percentage volume swelling	V_r
X_0	570	0.176
X_{25}	400	0.245
X_{75}	600	0.167
X_{125}	685	0.146

Figure 6 illustrates the stress-strain curves of a few blends of representative compositions. Evidently, tensile strength increases with increasing XNBR in the blend. It has been noted earlier in this paper, that the increase in XNBR concentration causes increased homogeneity of the blend.

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