Miscibility of self-vulcanizable rubber blend based on epoxidized natural rubber and chlorosulphonated polyethylene: effect of blend composition, epoxy content of epoxidized natural rubber and reinforcing black filler

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Dynamic mechanical analyses and differential scanning calorimetry studies show that the miscibility of a self-vulcanized blend of epoxidized natural rubber (ENR) and chlorosulphonated polyethylene (Hypalon) depends on the blend composition as well as the level of epoxidation in ENR. It has been found that ENR with 25 mol% epoxidation (ENR-25) forms completely miscible blends with Hypalon at all blend ratios. However, in the case of ENR with 50 mol% epoxidation (ENR-50), miscibility of the blend depends on blend composition. At lower ENR-50 loading the blend is immiscible, but at higher ENR-50 loading (i.e. 75/25 ENR-50/Hypalon) the blend becomes miscible. Miscibility is found to be unaffected by reinforcing black filler at 20 wt% loading.

(Keywords: self-vulcanizable rubber blends; miscibility; epoxidized natural rubber; chlorosulphonated polyethylene; blend ratio; epoxy content; reinforcing filler; dynamic mechanical analysis; differential scanning calorimetry)

INTRODUCTION

De and co-workers[1–6] have developed novel self-vulcanizable rubber blends based on rubbers with appropriate functional groups. Such blends are vulcanizable during moulding by the blend constituents themselves in the absence of any curatives and additives. Examples are blends based on epoxidized natural rubber (ENR) and carboxylated nitrile rubber[1,2], neoprene and carboxylated nitrile rubber[3], Hypalon and carboxylated nitrile rubber[4] and epoxidized natural rubber and Hypalon[5,6].

During further studies on blends based on ENR and Hypalon, it was observed that the extent of crosslinking reaction depends not only upon time and temperature of moulding but also on blend composition and extent of epoxy content in epoxidized natural rubber. These factors were found to affect the miscibility of the components in the blend. This paper reports the results of miscibility studies by dynamic mechanical analysis and differential scanning calorimetry with respect to blend ratio variation, epoxy content of epoxidized natural rubber and presence of reinforcing black filler.

EXPERIMENTAL

Details of the materials used and blend compositions are given in *Tables 1* and *2* respectively. The mixes are denoted by E_{100}, E_{75}, E_{50} and E_{25} corresponding to the weight percentage of ENR-50 in the blends. E_0 corresponds to 100 wt% of Hypalon-40. Similarly blends of ENR-25 and Hypalon are designated as E'_{100}, E'_{75}, E'_{50} and E'_{25}.

ENR and Hypalon were each masticated for 2 min on a 14″ × 6″ (355.6 mm × 152.4 mm) two-roll mixing mill to the same Mooney viscosity. They were then blended for about 4 min. For filled compounds, filler was added gradually after blending the two rubbers and then mixed thoroughly for a further 4 min. Total mixing time was about 8 min for unfilled systems and 12 min for filled systems. The blends were self-vulcanized by moulding for 60 min at 150°C.

Table 3 shows the formulations of the mixes involving single rubbers (Hypalon, ENR-25 and ENR-50). These were vulcanized at 150°C to optimum cure times as determined by the Monsanto Rheometer R-100.

The miscibility of ENR and Hypalon blends was investigated by differential scanning calorimetry (d.s.c.) and dynamic mechanical analysis (d.m.a.). Dynamic mechanical properties were measured using a Toyo-Baldwin Rheovibron model DDV-III-EP at a strain amplitude of 0.0025 cm and frequency of 3.5 Hz. The procedure was to cool the sample to −100°C and record the measurements during warm-up. The temperature rise was 1°C $\min^{-1}$.

D.s.c. measurements were made on a DuPont differential scanning calorimeter model 910 in nitrogen atmosphere. Glass transition temperatures (T_gs) of the samples were taken as the midpoint of the step in the scan, run at a heating rate of 20°C $\min^{-1}$.

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Table 1 Details of materials used

Materials	Characteristics	Source
Chlorosulphonated polyethylene	Trade name: Hypalon Grade: Hypalon-40	DuPont Ltd, USA
ENR-50	50 mol% epoxidized natural rubber	The Malaysian Rubber Producers Research Association, Brickendonbury, UK
ENR-25	25 mol% epoxidized natural rubber	The Malaysian Rubber Producers Research Association, Brickendonbury, UK
Carbon black	ISAF (N 220)	Philips Carbon Black Ltd, India

Table 2 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. 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 and Hypalon

Table 3 Formulations of single components

	E_{100}	E'_{100}	E_0
ENR-50	100	–	–
ENR-25	–	100	–
Hypalon	–	–	100
Sodium carbonate	0.25	0.25	–
Zinc oxide	5	5	–
Magnesium oxide	–	–	10
Stearic acid	2	2	–
Sulphur	0.3	0.3	–
MOR[a]	2.4	2.4	–
TMTD[b]	1.6	1.6	–
Tetrone A[c]	–	–	1.5

[a] *N*-Oxydiethylene benzothiazole-2-sulphenamide
[b] Tetramethyl thiuram disulphide
[c] Dipentamethylene thiuram tetrasulphide

RESULTS AND DISCUSSION

In order to examine the miscibility of ENR–Hypalon blends, the clarity of the films obtained by compression moulding for 60 min at 150°C was checked. The films were clear indicating that the polymer pairs were miscible. However, the film clarity test alone does not provide unequivocal proof regarding the miscibility of a polymer pair, since an immiscible polymer pair may yield clear films when the refractive indices of the two polymers are equal.

The final evidence in support of miscibility is available from glass transition temperature (T_g) studies. Dynamic storage modulus (E'), loss modulus (E'') and damping ($\tan\delta$) of different compositions of ENR–Hypalon blends are shown in *Figures 1* to *6*. Dynamic storage modulus rapidly decreases at the T_g zone due to the decrease in stiffness of the samples. Concomitantly, loss modulus and

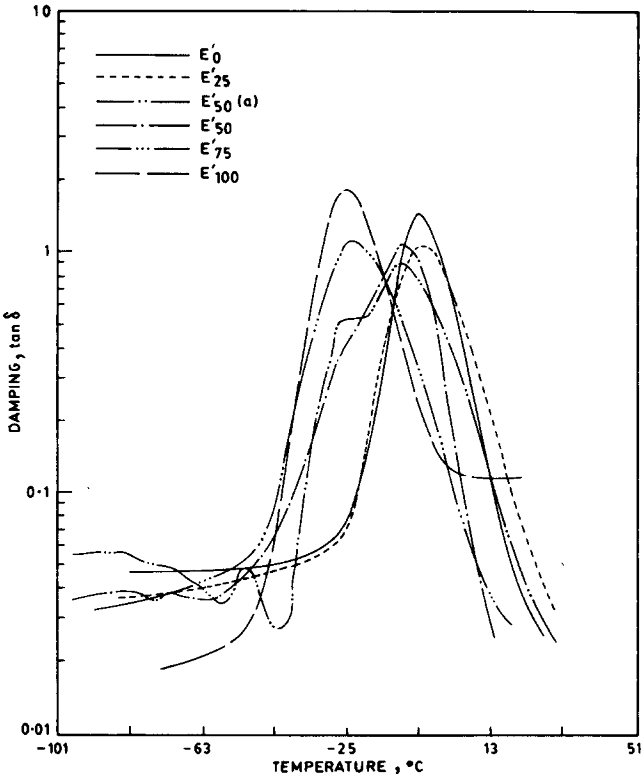

Figure 1 Mechanical damping ($\tan\delta$) of ENR-25, Hypalon and their blends at different temperatures. E'_{50} (a) indicates the 50/50 blend of ENR-25/Hypalon, moulded for 15 min at 150°C. Other blends were moulded for 60 min at the same temperature

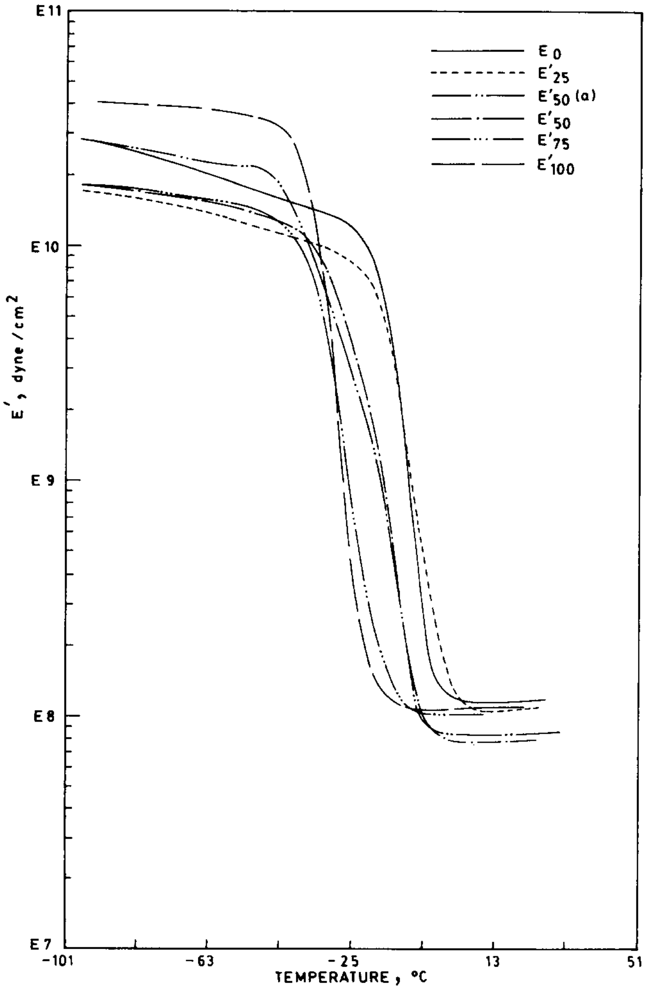

Figure 2 Storage modulus (E') of ENR-25, Hypalon and their blends at different temperatures

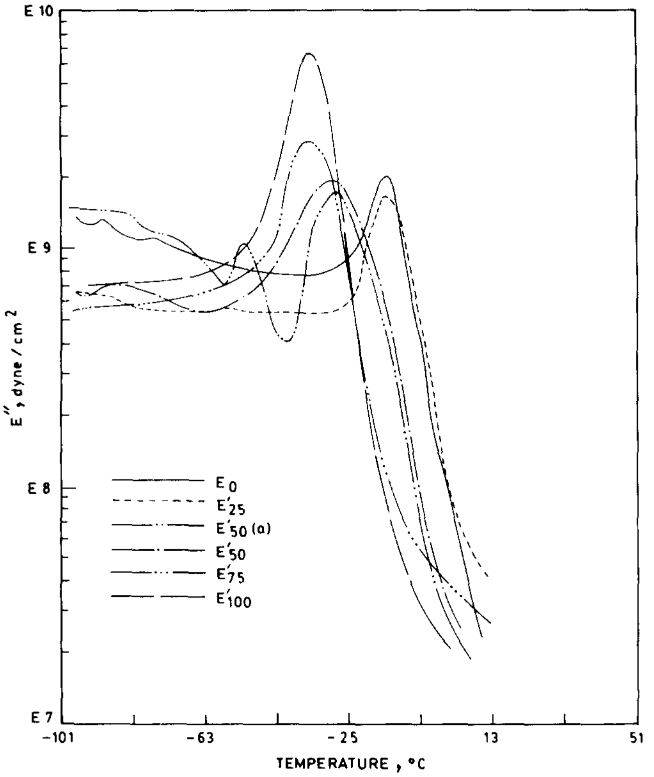

Figure 3 Loss modulus (E'') of ENR-25, Hypalon and their blends at different temperatures

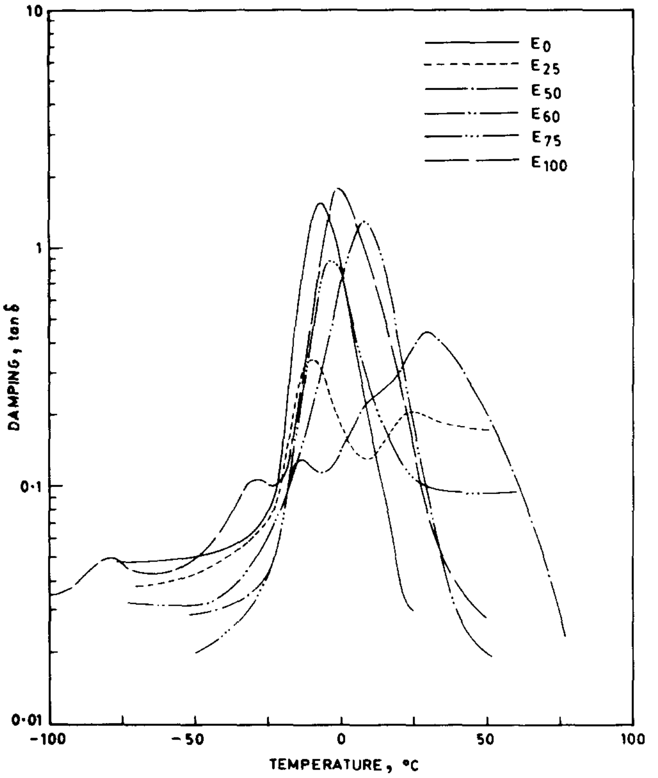

Figure 4 Mechanical damping (tan δ) of ENR-50, Hypalon and their blends at different temperatures

damping rise sharply to a maximum and then fall with increase in temperature. The temperature corresponding to the maximum in damping or loss modulus is taken as the T_g of the samples. As a general trend in polymer systems, the temperature corresponding to the loss modulus maximum in all cases is found to be lower than that of damping maximum.

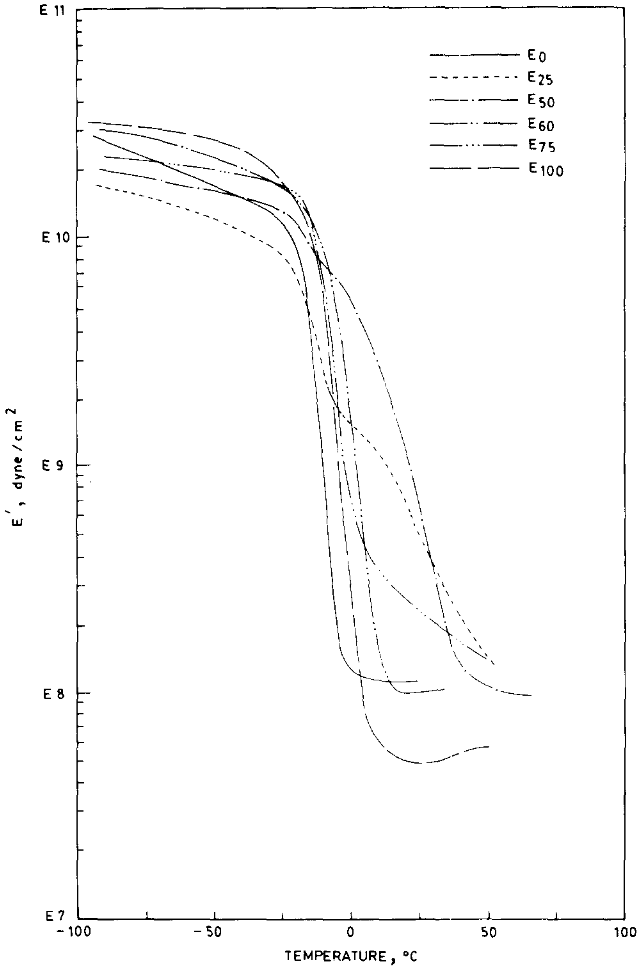

Figure 5 Storage modulus (E') of ENR-50, Hypalon and their blends at different temperatures

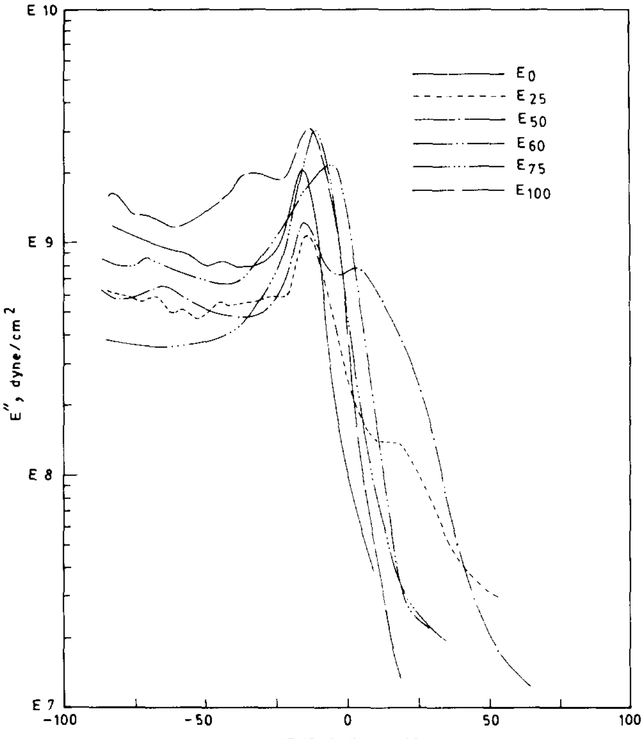

Figure 6 Loss modulus (E'') of ENR-50, Hypalon and their blends at different temperatures

Pure ENR-50 shows α-relaxation corresponding to glass–rubber transition (T_g) and β-relaxation due to motion of side groups in the glassy region, as seen from plots of viscous modulus and damping[7]. However, ENR-25 and Hypalon do not show any other transition in the glassy region other than T_g. The transition due to motions of side groups of ENR-50 is found to be absent in the blends of ENR-50 and Hypalon. It is reported that absence of secondary relaxation can be due to the interaction between the blend components[8,9].

From the plots of storage modulus, mechanical damping and loss modulus against temperature it is clear that miscibility of the two phases depends on the blend composition as well as on level of epoxidation in ENR. Blends of ENR-25 and Hypalon in all compositions exhibit only a single glass–rubber transition temperature (*Figures 1* to *3*), which occurs in between the T_gs of the single components. This indicates that the system is miscible at all compositions.

The effect of blend composition on T_g is shown in *Figure 7*. In each case the results have been compared with the commonly used Fox equation[10]:

$$1/T_{g_b} = W_1/T_{g_1} + W_2/T_{g_2} \tag{1}$$

where T_{g_b}, T_{g_1} and T_{g_2} are the T_gs of the blend, component 1 and component 2 respectively, and W_1 and W_2 are the weight fractions of components 1 and 2 respectively. The experimental values of T_g obtained by the three methods show deviation from linearity, which indicates a strong specific interaction between the polymers[11].

At higher level of epoxidation (50 mol%), as in ENR-50, phase separated blends with Hypalon are obtained, unless the ENR-50 content in the blends is more than 50 wt%. Two glass transitions for the blends of ENR-50/Hypalon with ratios 25/75 and 50/50, indicate the presence of two phases in the blends. The higher T_g should correspond to a phase composed principally of ENR-50, and the lower T_g corresponds to a phase wherein Hypalon is the major component. The T_gs of both phases depend on blend composition, and this is an indication that each polymer dissolves the other to an extent that depends on overall blend composition[12]. Again, movement of the T_gs away from the T_gs of single components indicates very strong interaction between the two phases[13].

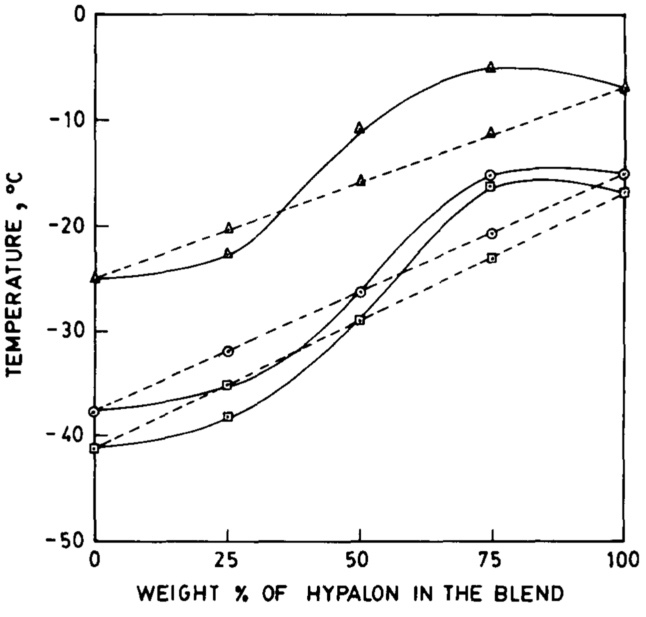

Figure 7 Effect of blend ratio on T_g of ENR-25/Hypalon blends. □, D.s.c. values; △, tan δ values; ○, E'' values; ------, Fox relationship

As the ENR concentration in the blends increases beyond 50 wt%, the blends become miscible, as is evident from the occurrence of single glass transition temperature (*Figures 4* to *6*). This suggests a single phase morphology in the blends. For the 75/25 ENR-50/Hypalon blend, T_g occurs in between the T_gs of the single components, whereas for the 60/40 blend (E_{60}) T_g shifts to a higher temperature, indicating a greater extent of crosslinking[13].

This system appears to be very similar to that of epoxy polymer/poly(vinyl chloride) (PVC) blend system[14], in which the system is immiscible at low PVC concentration (up to 10%), but becomes more miscible as the concentration of PVC increases. Feldman *et al.*[14] observed that in blends of low PVC concentration (up to 10%), the PVC is readily distinguishable as dispersed particles. However, at higher PVC concentration (about 50%), the blend consists of PVC particles containing a small proportion of epoxy polymer surrounded by a phase of well mixed epoxy polymer and PVC, and a phase of pure epoxy polymer. Thus the miscibility of two phases depends on the morphology of the system. Miscibility of ENR-50/Hypalon blends is likely to depend on similar factors.

From the above discussion, it is clear that the miscibility of ENR with Hypalon depends on the extent of epoxidation of the main chain of ENR. For example, ENR-25/Hypalon blends are miscible at all blend compositions, whereas ENR-50/Hypalon is miscible only when ENR-50 concentration is above 50 wt% in the blends. It has been reported[15] that chlorinated polyethylene forms a completely miscible blend with epoxidized polyisoprene when the main chain of the latter is epoxidized to 25 mol%, but phase separated blends are obtained with 50 mol% epoxidized polyisoprene. There are several examples in the literature[16–18] which show that by changing the solubility parameter of a polymer, either by chemical modification or by copolymerization with another monomer of different concentration, miscibility with other polymers could be altered.

In order to study the effect of the extent of crosslinking on the glass transition temperature and hence on miscibility, the 50/50 blend of ENR-25/Hypalon was moulded for 15 min at 150°C. The results are shown in *Figures 1* to *3*. The plot of damping against temperature shows a broad peak around −11.3°C with a shoulder region at around −21.3°C to −23.2°C and one minor transition of short scale motions of molecular chain segments at −53.3°C in the glassy region, which may be the result of structural defects in the material[7]. But when the same blend is moulded for 60 min, a single transition is observed indicating increase in miscibility of the system. This indicates that miscibility of the two phases is improved by the formation of covalent bonds between the components through crosslinking. Straight blending followed by crosslinking has led to increased miscibility in the case of styrene–butadiene rubber/polybutadiene rubber (SBR/BR)[19] and natural rubber (NR)/BR[20] systems. This demonstrates that crosslinking can induce increased solubility in polymer–polymer systems.

Additional evidence for the mutual solubility of ENR and Hypalon is obtained from d.s.c. thermograms, shown

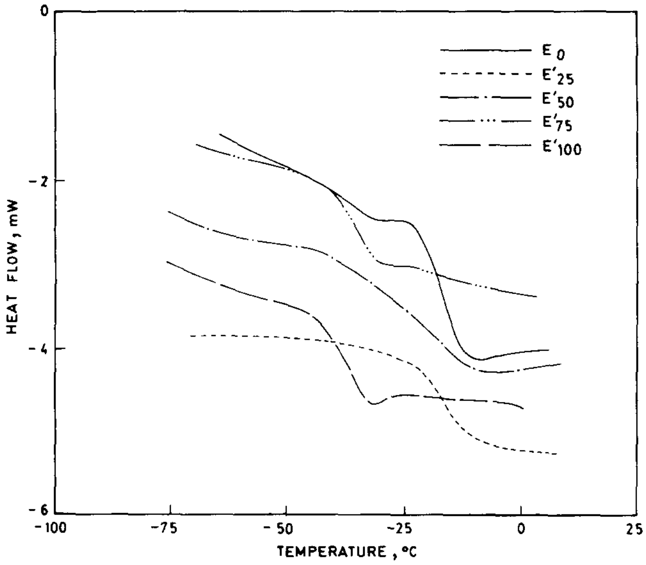

Figure 8 D.s.c. thermograms of ENR-25/Hypalon blends

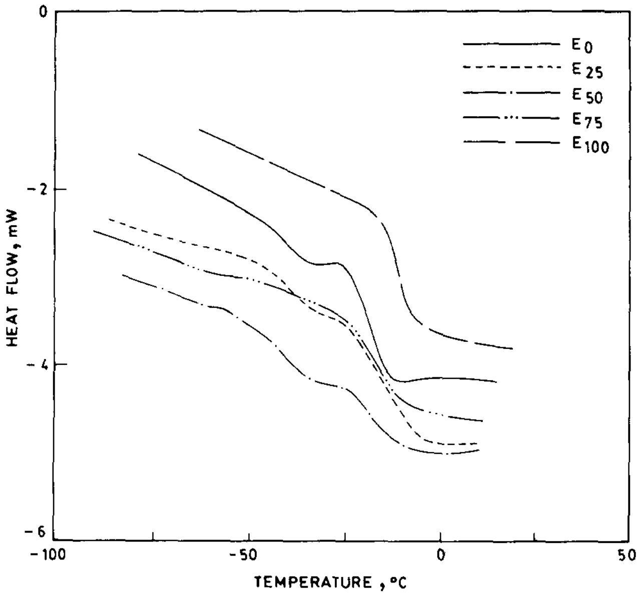

Figure 9 D.s.c. thermograms of ENR-50/Hypalon blends

in *Figures 8* and *9*. Glass transition temperatures of the blends, determined by different methods, are summarized in *Tables 4* and *5*.

Figures 10 to *15* show the effect of temperature on storage modulus, damping and loss modulus of the blends in presence of reinforcing ISAF carbon black filler at 20 wt% loading. *Figure 10* shows the tan δ spectra over the entire range of experimental temperatures (−100° to +51°C), for ENR-25/Hypalon blends. It is apparent from the spectra that the glass–rubber transition peak decreases on introduction of carbon black filler. It is also observed that the addition of filler broadens the transition peak as well as shifting it to a higher temperature (*Table 6*).

For blends of ENR-50 and Hypalon of composition 25/75 and 50/50, two transitions, similar to unfilled systems, were observed (*Figures 13* to *15*). For the 75/25 blend of ENR-50/Hypalon, broadening of the transition peak was observed on addition of filler.

Extensive investigations of the morphology of carbon black[21–24] have shown that the persistent, irreversible

Table 4 Glass transition temperatures (T_gs) of ENR-25/Hypalon blends obtained from differential scanning calorimetry (d.s.c.) studies and dynamic mechanical analysis (d.m.a.)

	T_g (°C)		
		Dynamic mechanical analysis	
Sample number	D.s.c.	Damping maxima, tan δ	Loss modulus maxima, E''
E'_{100}	−41	−25.4	−37.5
E'_{75}	−38	−23.2	−35.2
E'_{50}	−29	−11.2	−29.2
E'_{50}(a)	-	−11.3	−29.2 to −27.4
E'_{25}	−16	−5.2	−15.7
E_0	−17	−7.2	−15.3

Table 5 Glass transition temperatures (T_gs) of ENR-50/Hypalon blends, obtained from differential scanning calorimetry (d.s.c.) studies and dynamic mechanical analysis (d.m.a.)

	T_g (°C)		
		Dynamic mechanical analysis	
Sample number	D.s.c.	Damping maxima, tan δ	Loss modulus maxima, E''
E_{100}	−14	0	−9.2
E_{75}	−16	−3.2	−11.2
E_{60}	-	+6.7	−5.4
E_{50}	−18, −39	−13.2, +28.6	−15.3, −5.2 to −1.3
E_{25}	−14, −34	−9.3, +28.8	−13.3, +8.6 to +16.8
E_0	−17	−7.2	−15.3

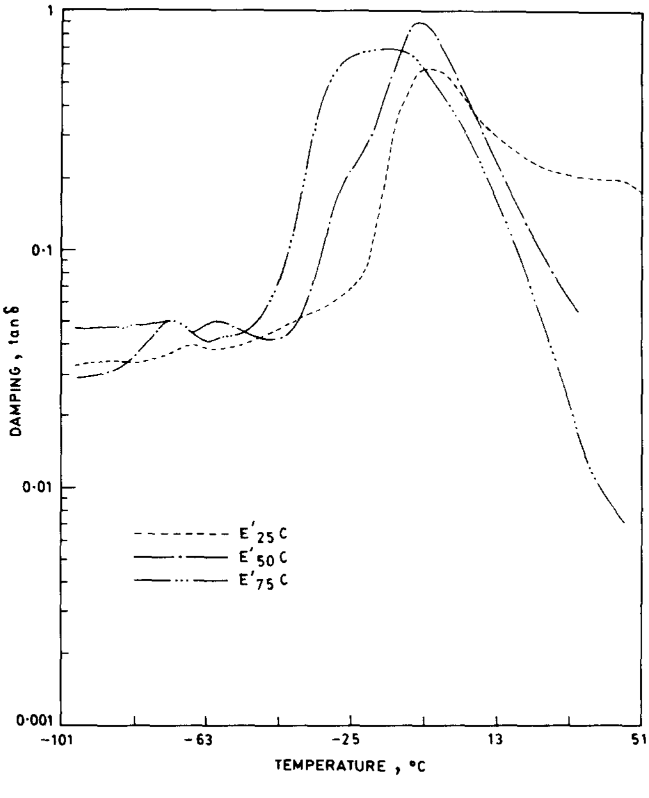

Figure 10 Mechanical damping (tan δ) of carbon black filled ENR-25/Hypalon blends at different temperatures

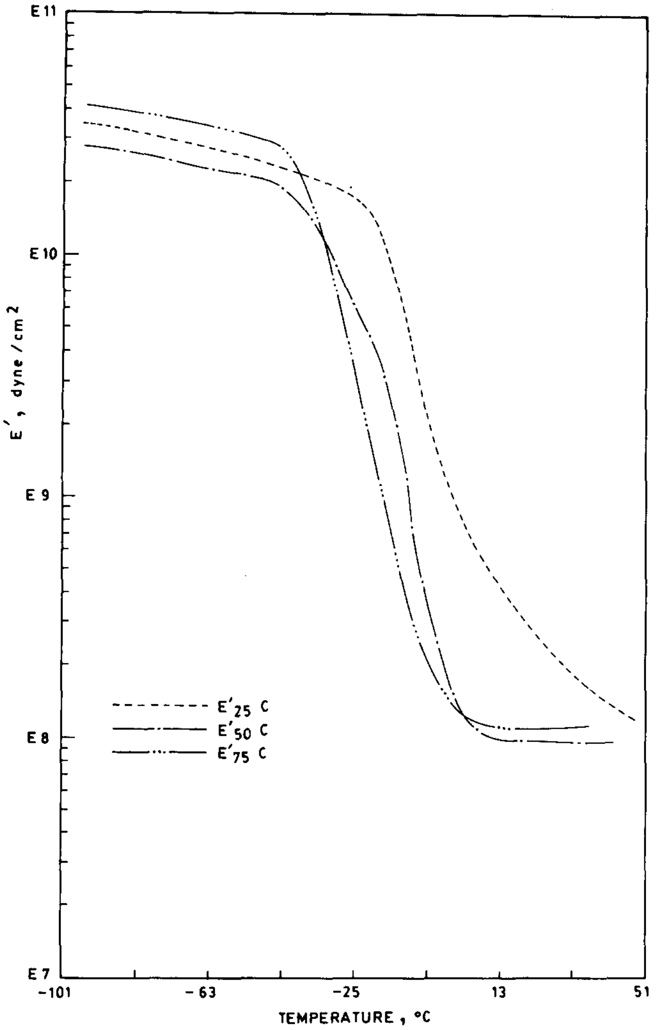

Figure 11 Storage modulus (E') of carbon black filled ENR-25/Hypalon blends at different temperatures

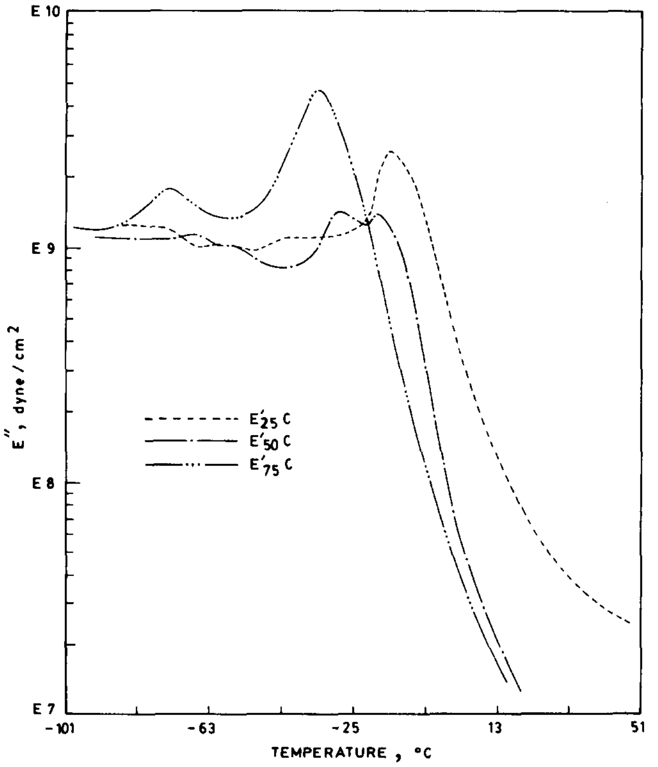

Figure 12 Loss modulus (E'') of carbon black filled ENR-25/Hypalon blends at different temperatures

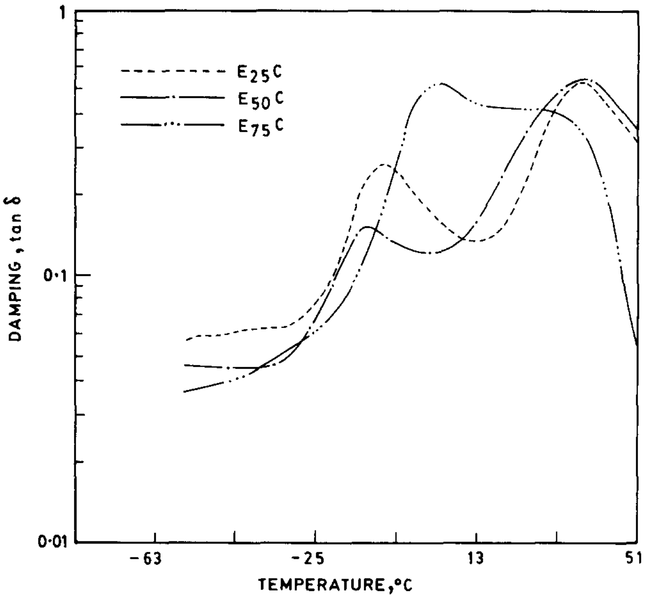

Figure 13 Mechanical damping (tan δ) of carbon black filled ENR-50/Hypalon blends at different temperatures

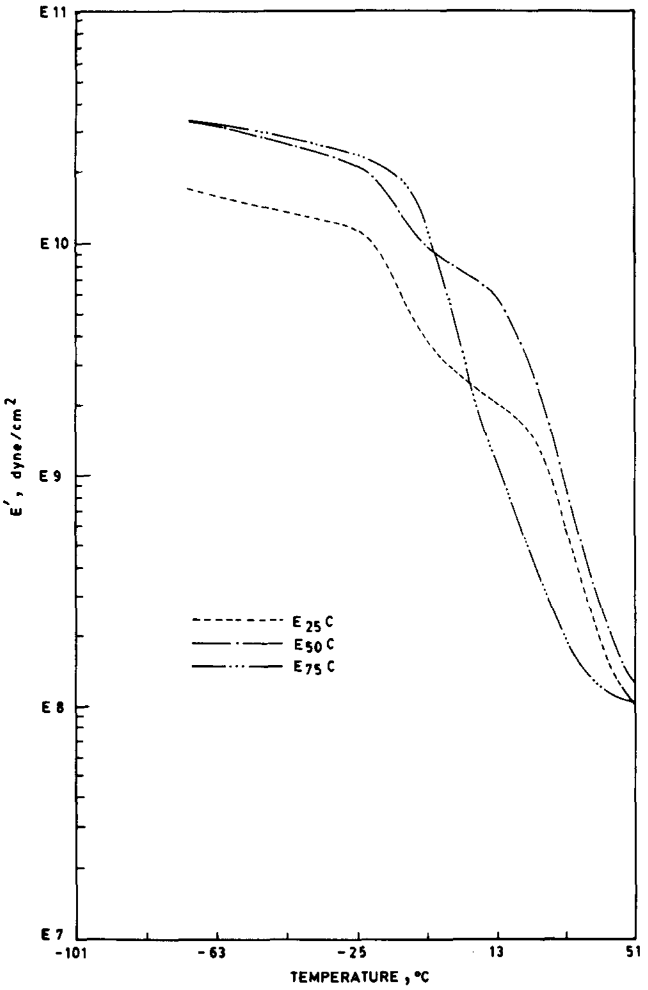

Figure 14 Storage modulus (E') of carbon black filled ENR-50/Hypalon blends at different temperatures

primary structure originates from reticular particle aggregates, which appear to be fused together in the formative stage of carbon black at extremely high temperature in the furnace. Investigation by Medalia[25] and Kraus[26] have shown that polymer occluded within the internal void space of the primary structure aggregate

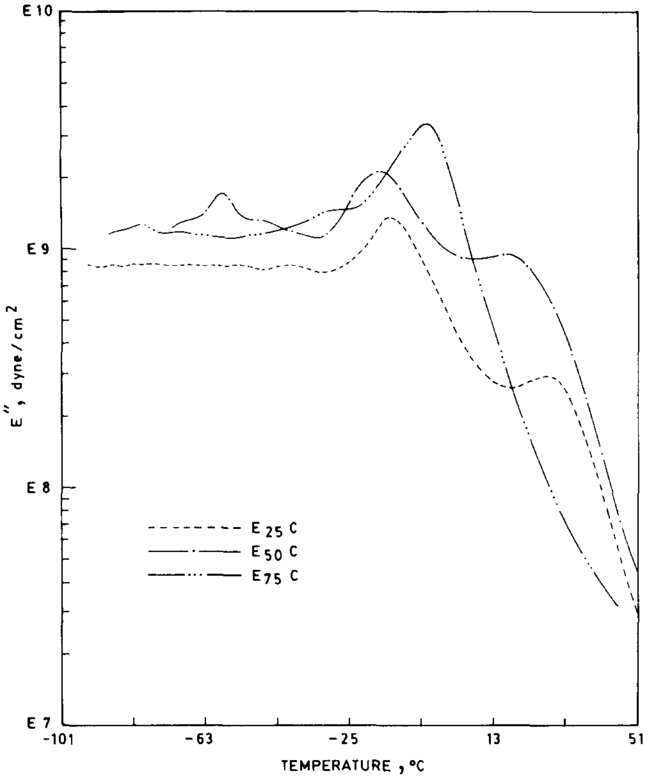

Figure 15 Loss modulus (E'') of carbon black filled ENR-50/Hypalon blends

Table 6 Effect of filler on glass transition temperatures (T_gs) of ENR/Hypalon blends, obtained from dynamic mechanical analysis (d.m.a.)

	T_g (°C)	
Sample number	Damping maxima, tan δ	Loss modulus maxima, E''
$E_{75}C$	+2.5 to +4.7 (broad maxima)	−5.2
$E_{50}C$	−13.8, +38.8	−15.7, +12.8 to +16.9 (broad maxima)
$E_{25}C$	−9.3, +38.7	−15.3, +26.6
$E'_{75}C$	−25 to −11.1 (broad maxima)	−33.7
$E'_{50}C$	−7.2	−29.4 to −19.2 (broad maxima)
$E'_{25}C$	−5.2	−15.4

is not free to fully share in the macroscopic deformation of a carbon black filled rubber. Some investigators[27,28] identified this immobilized rubber with "bound rubber" measured by solvent extraction, whereas others, through microscopic study[29,30], modulus[31] and tensile measurements[32–34], indicated the existence of a shell of immobilized rubber of definite thickness around vulcanizate. Medalia[35] suggested that the independent nature of occluded rubber, bound rubber and shell rubber may result in them overlapping each other, forming a complicated interlinked system. Thus, filled polymers constitute a system with a complex structure of two components, the absorbed hard rubber and the bulk rubber. The absorbed, hard, immobilized rubber would cause a perturbed relaxation response. Then the tan δ peak may be ascribed to the glass transition relaxation of the bulk rubber and thus the tan δ peak decreases on introduction of carbon black.

A shift of relaxation spectra to higher temperature with the addition of reinforcing filler has been reported by many workers[36–38]. This is also due to the formation of immobilized layers on the filler surface. The broad maxima may be attributed to the superposition of different relaxation processes.

CONCLUSIONS

The miscibility of ENR/Hypalon blends depends on the level of epoxidation in epoxidized natural rubber as well as on its proportion in the blend. Crosslinking enhances the miscibility of the two components. Reinforcing filler at 20 wt% has no effect on miscibility, but causes reduction in tan δ peak height and a broad maximum which is shifted to a higher temperature.

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