Thermally induced crosslinking in the immiscible blend of zinc sulfonated ethylene–propylene–diene monomer rubber and epoxidized natural rubber

N. R. Manoj, S. K. De and P. P. De*
Rubber Technology Center, Indian Institute of Technology, Kharagpur 721 302, India

and D. G. Peiffer
Exxon Research & Engineering Company, Route 22 East, Clinton Township,
NJ 08801, USA
(Received 20 July 1992)

Intermolecular chemical interactions between the sulfonate and epoxy groups at high temperatures make the blend of the zinc salt of sulfonated ethylene–propylene–diene monomer rubber (sEPDM) and epoxidized natural rubber (ENR) a self-crosslinkable system, as studied by Monsanto rheometry, dynamic mechanical and infra-red analyses. The blend components are immiscible due to the structural changes taking place in ENR during the chemical reaction, and the predominance of non-interacting and non-ionic regions. Infra-red studies confirm that the crosslinked network consists mainly of sulfonate ester and ether linkages.

(Keywords: ethylene–propylene–diene monomer; sulfonation; zinc salt; ionomer; epoxidized natural rubber; blend; self-crosslinking; immiscibility)

INTRODUCTION

Ionic polymers or ionomers, which contain low concentrations of pendent ionic groups, exhibit unique properties that result from the association or aggregation of the ionic groups dispersed in the matrix[1–5]. The resultant polymer properties are found to be dependent on the ionic content, degree of neutralization and type of cation. Polymers containing sulfonate groups, neutralized by metal counterions, especially sulfonated ethylene–propylene–diene monomer rubber (sEPDM) and sulfonated polystyrene (sPS), have gained special interest because of their unique properties arising from the strong ionic interactions as compared to other ionic groups[2]. These ionomers are in a sense heterogeneous since these interactions lead to the formation of ionic multiplets, aggregates, clusters or inverted micelles, which are distributed non-uniformly in the non-polar matrix[6]. Both sEPDM and sPS show pronounced ionic aggregation even at sulfonate levels $\geqslant 15$ meq/100 g of polymer[7]. These interactions can be modified by a polar additive through specific solvation of the metal ion groups[8].

These ionomers produce interesting blends with some polymers. Xie and Ma have reported the blends of sEPDM with polypropylene, polyethylene, poly(vinyl chloride), poly(ethylene oxide) and sulfonated butyl rubber, which exhibit additive, synergistic or antagonistic behaviour in properties[9,10]. Ionic interactions can yield compatible blends of otherwise incompatible polymers, especially by the incorporation of acidic groups (SO_3H) in one polymer and a non-ionic basic group (vinylpyridine) in the other[11,12]. Miscibility in blends of polyamide-6 and manganese sulfonated polystyrene has been attributed to specific interactions[13].

Self-crosslinkable plastic–rubber and rubber–rubber blends form a set of unique polymer mixtures, which can crosslink on their own without the aid of any external agents during high-temperature moulding, through the chemical interaction of the functional groups present in the individual polymers[14–20]. A large number of polymer blends have been identified as self-crosslinkable, which include carboxylated nitrile rubber (XNBR)/epoxidized natural rubber (ENR)[14], chlorosulfonated polyethylene/XNBR[17], polychloroprene/ENR[15], poly(vinyl chloride) (PVC)/ENR[18] and PVC/NBR[20]. These blends interact chemically at high temperatures during moulding and form crosslinks by condensation or substitution reactions. Since the reaction necessitates chemical moieties that can interact, ionomers are likely to be interesting in such blend systems.

This paper deals with the results of studies on the blend of sEPDM and ENR, with special reference to the thermally induced crosslinking reaction between the individual polymers in the absence of external agents.

---

* To whom correspondence should be addressed

0032-3861/93/102128-07

EXPERIMENTAL

The details of the materials used are given in *Table 1*.

Blending

The different blends were prepared in a tight-nipped two-roll mill at 30°C. First ENR was masticated for 2 min and then sEPDM was added. Mixing was continued for another 5 min and the blend was then sheeted out.

Characterization of the blends

Monsanto rheographs of the different blends were taken in a Monsanto Rheometer R 100. The blends were moulded in a hydraulic press at 170°C.

Swelling studies were done in a solvent mixture of hexane/ethanol/tetrahydrofuran (50/10/40) at 30°C for 48 h.

The dynamic mechanical studies were performed in a Rheovibron DDV III-EP viscoelastometer at a frequency of 3.5 Hz. Experiments were conducted at a double strain amplitude of 0.25% over a temperature range of −100 to +200°C, at a heating rate of 2°C min^{-1}.

A Seiko DSC 220 C calorimeter equipped with a data-station was used to obtain the thermal transition behaviour of the blends. A heating rate of 20°C min^{-1} was used in all cases.

The infra-red (i.r.) spectra of the materials were acquired on thin moulded (2 and 60 min, at 170°C) films using a Mattson Polaris *FT*i.r. spectrophotometer. The scan resolution was 2 cm^{-1}, and a minimum of 100 scans were accumulated for each spectrum at a scan rate of 5.74 s per scan.

Table 1 Details of the materials

Designation	Description	Source
sEPDM	Zinc salt of sulfonated ethylene–propylene–diene monomer rubber Ethylene: 50% 5-Ethylidine-2-norbornene: 5% Sulfonation: 25 meq/100 g polymer ML (1+4), 100°C: 25	Exxon Research & Engineering Company, New Jersey, USA
ENR	Epoxidized natural rubber 50 mol% epoxidation ML (1+4), 100°C: 59	Kumpulan Gutheric Berhad, Malaysia

RESULTS AND DISCUSSION

Monsanto rheometric studies

Rheographs of the blends at different temperatures and blend ratios are shown in *Figures 1* and *2*. The gradual rise in the torque value with time of the 50/50 blend of sEPDM and ENR (*Figure 1*) indicates crosslinking between the two rubbers at 170°C. The possibility of thermovulcanization of the individual rubbers is eliminated since the neat polymers do not register any such rise in torque. In the absence of sulfonate or epoxy groups in the backbone chain, as in the blends of sEPDM/NR and EPDM/ENR, no increase in torque with time was observed, confirming the contention that the rise in torque is due to the chemical interaction of the sulfonate and epoxy groups in the rubbers. *Figure 1* also illustrates the effect of variation of blend ratio, where the 75/25 sEPDM/ENR blend registers the highest torque and the 25/75 blend registers the minimum. This shows that the extent of crosslinking depends largely on the concentration of sEPDM.

Figure 2 shows the rheographs of the 50/50 blend of sEPDM and ENR at different temperatures. As expected, the rate and extent of the crosslinking reaction increase with temperature. At 190°C, however, reversion (or decrease in torque) starts after 40 min, presumably due to thermal degradation of the crosslinked structure.

Swelling studies

The swelling studies give further evidence for the crosslinking reaction. Whereas the individual rubbers are soluble in a common solvent (a 50/10/40 n-heptane/ethanol/tetrahydrofuran mixture), the 50/50 and 75/25 blends moulded for 60 min swell only to a limited extent. The 25/75 blend moulded for 60 min and all the blends moulded for 2 min are soluble, showing the very low degree of crosslinking in these blends. The results are summarized in *Table 2*.

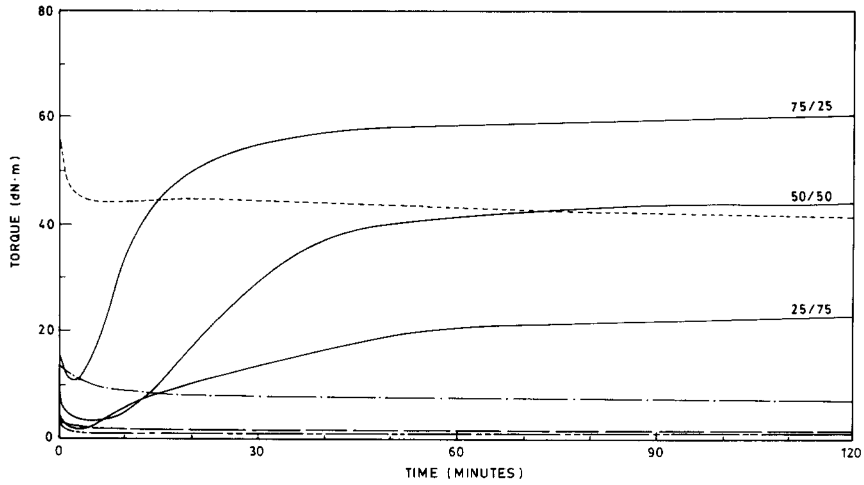


Figure 1 Rheographs of the sEPDM/ENR blend system at different blend ratios: sEPDM (-----); ENR (—————); sEPDM/ENR blends (——); 50/50 NR/sEPDM (—·—); and 50/50 ENR/EPDM (– – –)

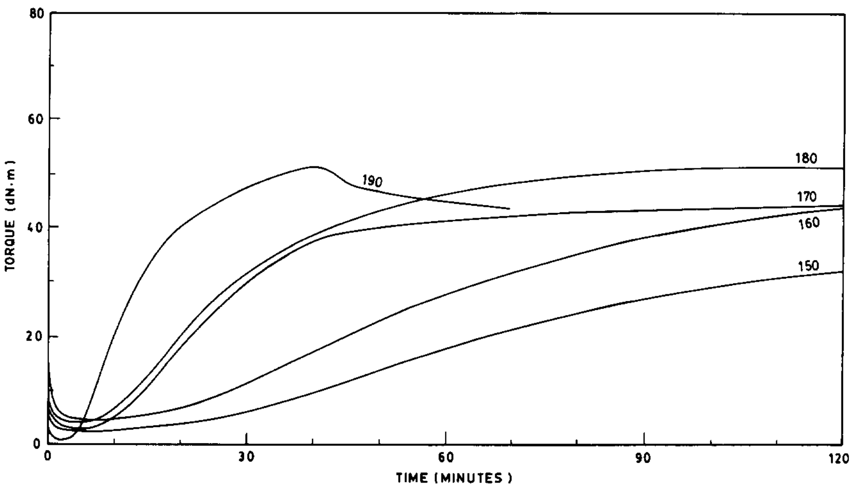


Figure 2 Rheographs of the 50/50 sEPDM/ENR blend at different temperatures (°C)

Table 2 Swelling characteristics of sEPDM/ENR blend in n-heptane/ethanol/tetrahydrofuran (50/10/40) at 30°C

Composition sEPDM/ENR	Moulding time (min)	Increase in weight (%)
100/0	2	[a]
25/75	2	[a]
	60	[a]
50/50	2	[a]
	60	343
75/25	2	[a]
	60	214
0/100	2	[a]

[a] Soluble

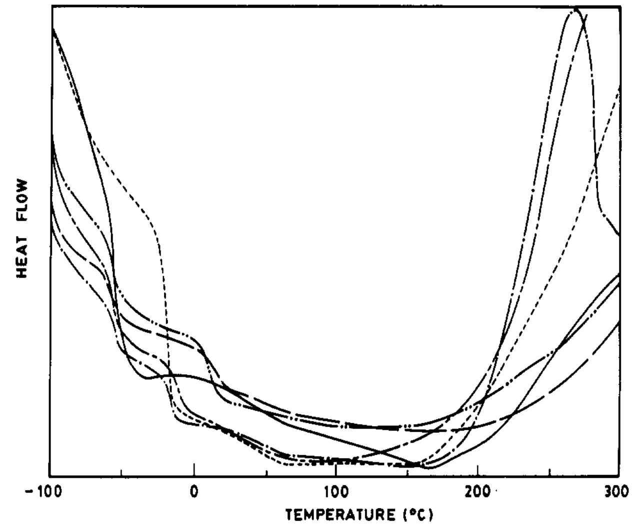


Figure 3 D.s.c. thermograms of the single rubbers and 50/50 sEPDM/ENR blends: sEPDM (——); ENR (----); 50/50 blends moulded for 2 min (—·—), 2 min, second heating (—··—), 60 min (———) and 60 min, second heating (— — —)

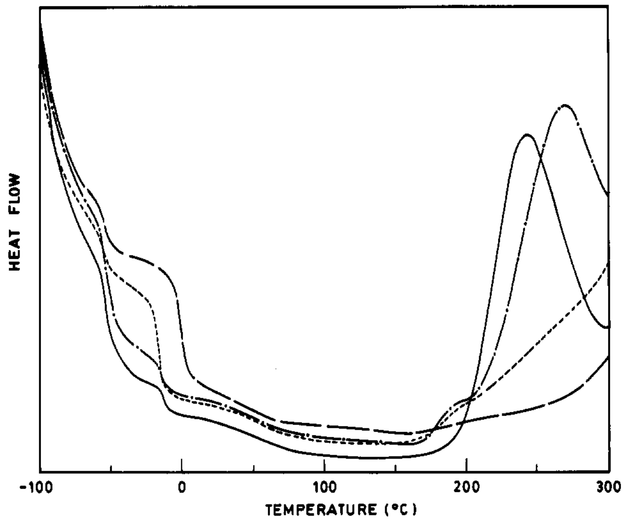


Figure 4 D.s.c. thermograms of the 75/25 and 25/75 sEPDM/ENR blends: 25/75 blend moulded for 2 min (——) and 60 min (---); and 75/25 blend moulded for 2 min (—·—) and 60 min (— — —)

D.s.c. studies

The d.s.c. thermograms of the blends are shown in *Figures 3* and *4*. The midpoint of the inflection in the curves was taken as the glass transition temperature (T_g) and the results are summarized in *Table 3*. sEPDM and ENR show glass transitions at -55 and -17°C, respectively. All the blends, irrespective of the moulding times, exhibit two distinct transitions, showing the immiscibility of the components. *Figure 3* shows the thermal behaviour of the 50/50 blend moulded for 2 and 60 min. There is a slight shift in the T_g of ENR, from -16 to -11.5°C, whereas that of sEPDM remains the same. This change in T_g can be ascribed to the structural changes occurring in ENR during crosslinking. It is known that phase inhomogeneity due to ring-opened products or other changes in ENR is readily observable in the broadening and shifting of the transition[21]. This is evident in the thermograms obtained during the second heating, where the T_g of ENR shifted significantly. Since the first heating was carried out up to 300°C, the extent of reaction was high, resulting in more structural changes in ENR, and the shift in T_g. There is almost no shift in the case of the 25/75 blend moulded for 60 min, whereas the 75/25 blend registers a significant shift (*Figure 4*). This is in accord with the rheometric studies, where it was found that the extent of reaction was the highest in the 75/25 blend. In all cases there is no change in the T_g of sEPDM since this represents the softening of the ion-free backbone[22], which is not involved in the chemical interaction.

The exothermic peak in the high-temperature zone (at ca. 250°C) represents the crosslinking reaction. On

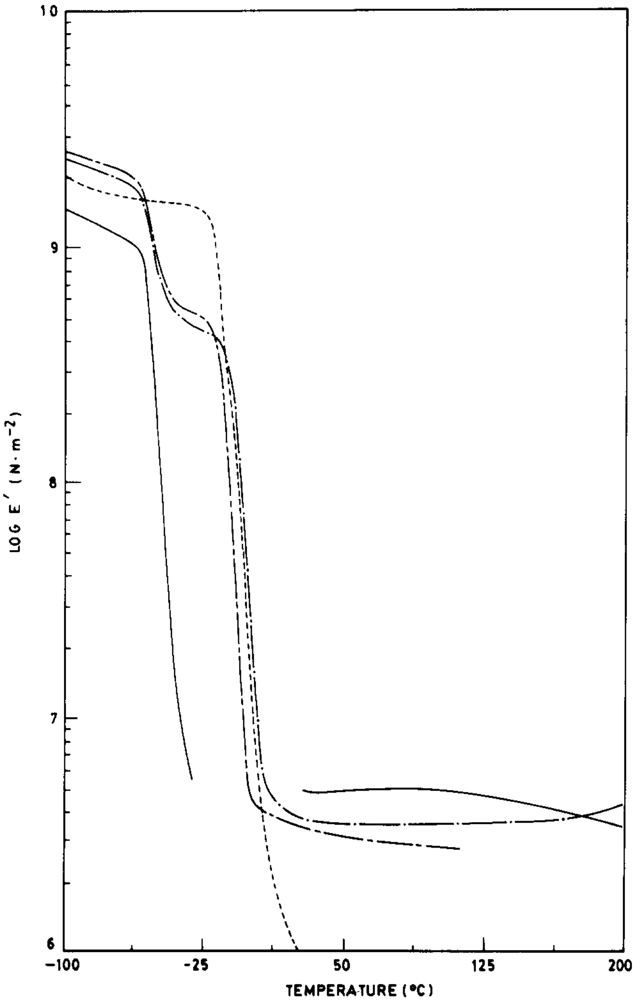


Figure 5 Semilogarithmic plots of storage modulus (E') vs. temperature of the single rubbers and 50/50 sEPDM/ENR blends: sEPDM (——); ENR (----); 50/50 sEPDM/ENR blends moulded for 2 min (— - —) and 60 min (— · —)

comparing the 2 and 60 min moulded blends, it can be seen that the exothermic peak diminishes after 60 min moulding, since some extent of reaction has already taken place during moulding. *Figure 3* also shows the drastic reduction in the peak height of the 50/50 blends after the second heating, indicating that considerable reaction did occur during the first heating itself.

Dynamic mechanical analyses

Figures 5–8 show the plots of storage modulus (E') and loss tangent ($\tan\delta$) *versus* temperature for the individual rubbers and the blends. While the single rubbers were moulded for 2 min, the blends were moulded for 2 and 60 min. The peak positions corresponding to the loss modulus and $\tan\delta$ maxima may be taken as the T_g, and the results are summarized in *Table 3*. The viscoelastic behaviour of sEPDM[22,23] and ENR[21,24,25] has been studied extensively. sEPDM has a glass transition temperature around −45°C and ENR at −1°C. While ENR displays viscous flow above its T_g, sEPDM shows the characteristic rubbery plateau extending up to 200°C, due to the ionic aggregates, which provide a temperature-resistant network in the form of ionic multiplets and clusters[22]. Above a critical ion concentration, ionic groups aggregate to form multiplets and clusters. Multiplets result from ion-pair interactions involving contact ion pairs whereas clusters contain ion-pair aggregates interspersed with polymer backbone chains[26].

Dynamic mechanical analyses show that the blends are immiscible since they exhibit two relaxations corresponding to the individual rubbers. The storage modulus plots show two transitions, whereas the loss tangent curves show two peaks. As observed earlier in the d.s.c. studies, the ENR peak shifts to higher temperatures on crosslinking, presumably due to the structural changes taking place in ENR. In the case of the 75/25 sEPDM/ENR blend, the shift in T_g is around 27°C, whereas there is no shift in the T_g of ENR in the 25/75 blend, confirming the greater extent of reaction in the former.

The rubbery plateau is also modified by the crosslinking reaction, as seen from *Figures 5* and *7*. The crosslinking results in an increase in the magnitude of the modulus at the plateau region in the case of the 50/50 and 75/25 sEPDM/ENR blends, which is in accordance with the theory of rubber elasticity[27]. In the case of the uncrosslinked 25/75 blend, viscous flow started at 25°C, whereas on moulding for 60 min the rubbery region extends up to 80°C, showing that the crosslinking reaction takes place even though it does not result in the shift of the ENR glass transition. Since the rubbery plateau is not greatly affected, it may be inferred that the clusters and multiplets remain intact even after crosslinking. It is possible that, at high moulding temperatures, the ionic aggregates become unstable and some of them may even redistribute during the chemical reaction. It has long been recognized that ion pairs reorient themselves from one aggregate to another, the rate of which controls its flow[28,29].

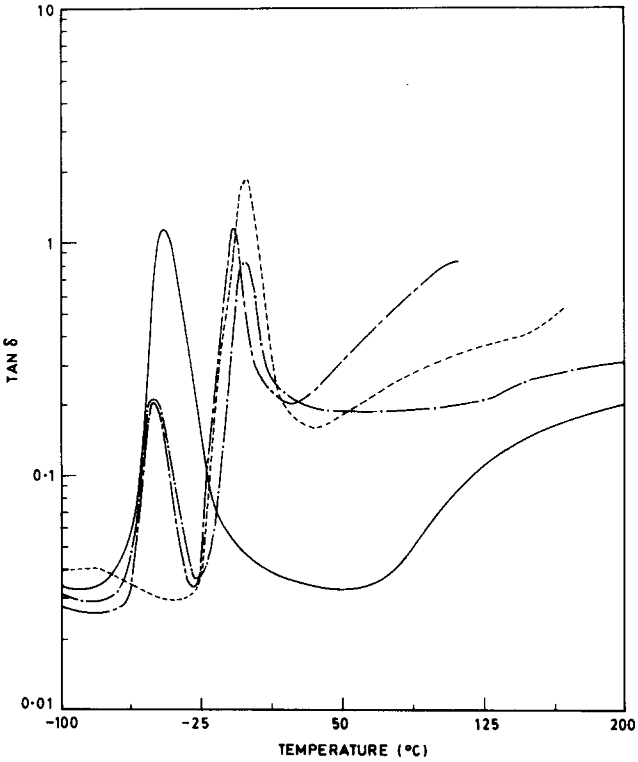


Figure 6 Semilogarithmic plots of loss tangent vs. temperature of the single rubbers and 50/50 sEPDM/ENR blends (curves are the same as in *Figure 5*)

The reasons for the existence of a peak at 99°C in the case of the 75/25 sEPDM/ENR blend moulded for 2 min,

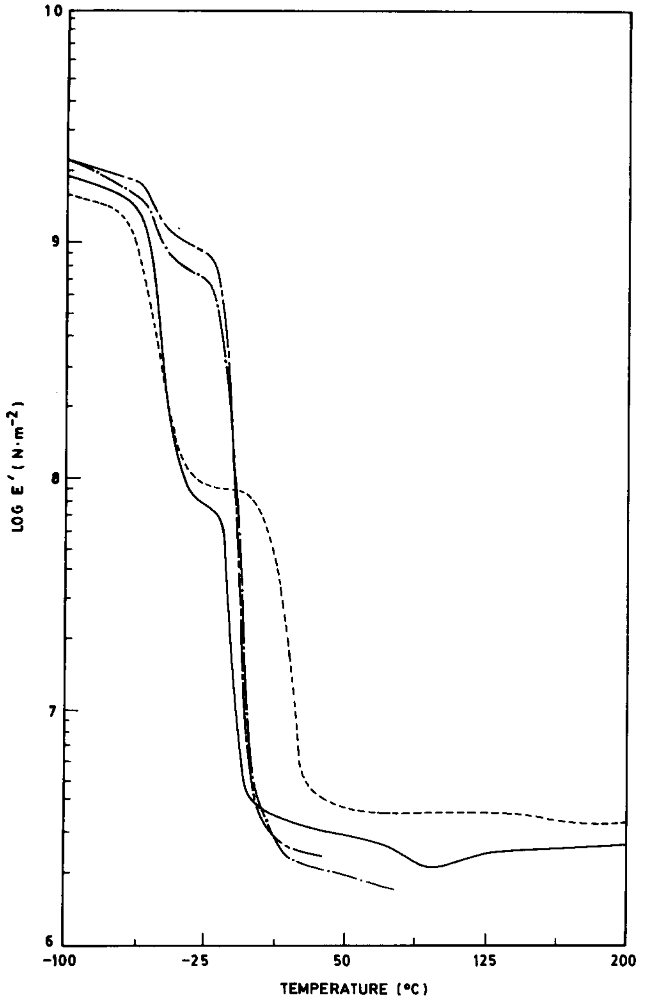


Figure 7 Semilogarithmic plots of storage modulus (E') vs. temperature of the sEPDM/ENR blends: 25/75 blend moulded for 2 min (——) and 60 min (----); and 75/25 blend moulded for 2 min (— — —) and 60 min (—·—)

and the downward shift of the T_g of ENR in the blends (observable in 2 min moulded blends) as compared to the single rubbers, are not understood.

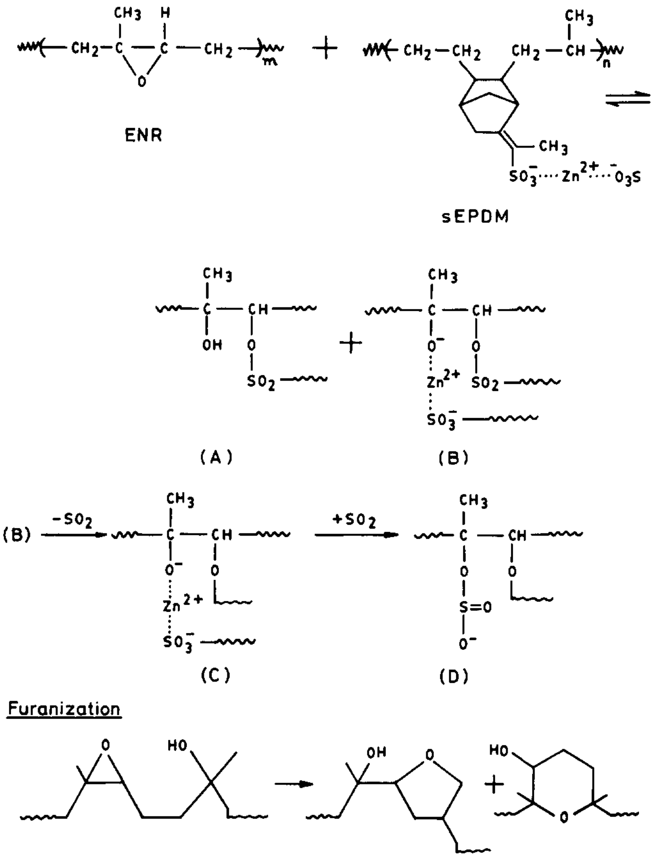
I.r. analysis

The formation of new bonds is evident in the infra-red spectra (*Figure 9*). The two spectra correspond to the 50/50 blends, moulded for 2 and 60 min and normalized in the 500 cm^{-1} region. The major characteristic peaks are summarized in *Table 4*.

The characteristic peaks of ENR are observed at 877 and 1250 cm^{-1}, and those of sEPDM at 1065, 1115 and 1160 cm^{-1}. The reduction in the absorbance at 877 cm^{-1} points to the decrease in the epoxy content due to crosslinking. The increase in the absorption at 1026, 1065, 1115 and 1160 cm^{-1} and the merging of the first three peaks establish the formation of ethers—both aliphatic and cyclic. The formation of ketones on ring opening of epoxides is known[32] and it is manifested here in the increased absorbance at 1732 cm^{-1}. The 1250 cm^{-1} peak is not affected, though the epoxy concentration decreases, because furans (cyclic ethers) also absorb in that region. The broadening and increased absorbance at 3250–3600 cm^{-1} show the formation of hydroxyl groups, which remain intermolecularly hydrogen bonded.

Crosslinking mechanism

It is well known that carboxylic acids attack epoxides to produce monoesters of 1,2-diols[33]. Carboxylated nitrile rubber has been shown to interact chemically with epoxidized natural rubber, resulting in ester linkages[14]. Since sulfonic acids are stronger acids than carboxylic acids, it is expected that a sulfonate ionomer can interact strongly with ENR. It has been shown that sulfenic acids and sulfoxides can cause ring opening of epoxides[34]. The nucleophilic attack on the carbon-bearing epoxy group is among the easiest epoxide reaction to occur[35,36]. Based on these facts and the results of the present studies, a probable reaction pathway is shown in *Scheme 1*.



Scheme 1

The reversibility of the first reaction is justified since sulfonate anion is known to be a good leaving group also. The reaction may thus result in the formation of sulfonate ester (A), new ionic groups (B), ether (C) through the exclusion reaction of SO_2 from a sulfonate ester or sulfite groups, and sulfite (D) linkages. The presence of bound water molecules and traces of acetic acid that may be retained in the polymer during manufacture[30] can catalyse the reactions. The formation of diols will lead to the furanization of ENR, if there are two adjacent epoxy rings (*Scheme 1*). This furanization and epoxy ring opening cause the shift in the glass transition peak of ENR (*Figures 3–8*). The T_g of sEPDM is not affected since the non-polar, ion-free backbone is not involved in any type of interactions. The increase in the modulus, which extends to even higher temperatures in the case of the crosslinked blends, could be due to the formation of the new ionic linkages, $-O^{-}\cdots Zn^{2+}\cdots SO_3^{-}-$ (C in *Scheme 1*), though it needs further analysis to confirm its existence.

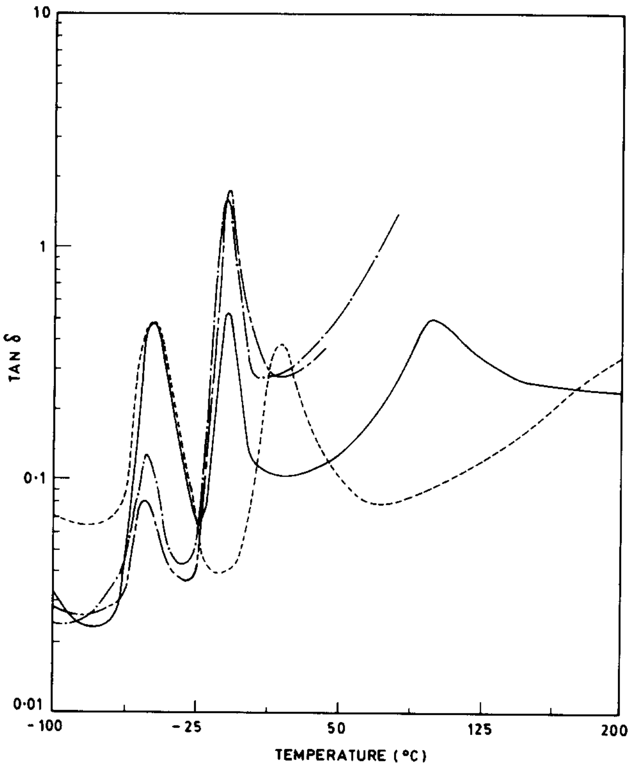


Figure 8 Semilogarithmic plots of loss tangent vs. temperature of the 75/25 and 25/75 sEPDM/ENR blends (curves are the same as in *Figure 7*)

CONCLUSIONS

The blend of zinc sulfonated EPDM and ENR is self-crosslinkable. The chemical interaction between the sulfonate and epoxy groups during high-temperature moulding leads mainly to the formation of ether and sulfonate ester linkages. The extent of crosslinking depends on the moulding temperature and blend ratio. The blend components are immiscible as seen from d.s.c. and dynamic mechanical analyses. The ENR transition peak shifts to higher temperatures due to the structural changes in ENR that occur during crosslinking.

REFERENCES

1 Eisenberg, A. and King, M. 'Ion-Containing Polymers', Academic Press, New York, 1977

2 Eisenberg, A. 'Ions in Polymers', Adv. Chem. Ser. 187, American Chemical Society, Washington, DC, 1980

3 MacKnight, W. J. and Lundberg, R. D. *Rubber Chem. Technol.* 1984, **57**(3), 652

4 Eisenberg, A. and Bailey, F. E. (Eds.) 'Coulombic Interactions in Macromolecular Systems', ACS Symp. Ser. 302, American Chemical Society, Washington, DC, 1986

5 MacKnight, W. J. and Earnest, Jr, T. R. *J. Polym. Sci., Macromol. Rev.* 1981, **16**, 41

6 Mauritz, K. A. and Hopfinger, A. J. 'Modern Aspects of Electrochemistry' (Eds. J. O'M. Bockris, B. E. Conway and R. E. White), Plenum, New York, 1982, Ch. 6

7 Fitzgerald, J. J. and Weiss, R. A. *J. Macromol. Sci.–Rev. Macromol. Chem. Phys.* (*C*) 1988, **28**(1), 99

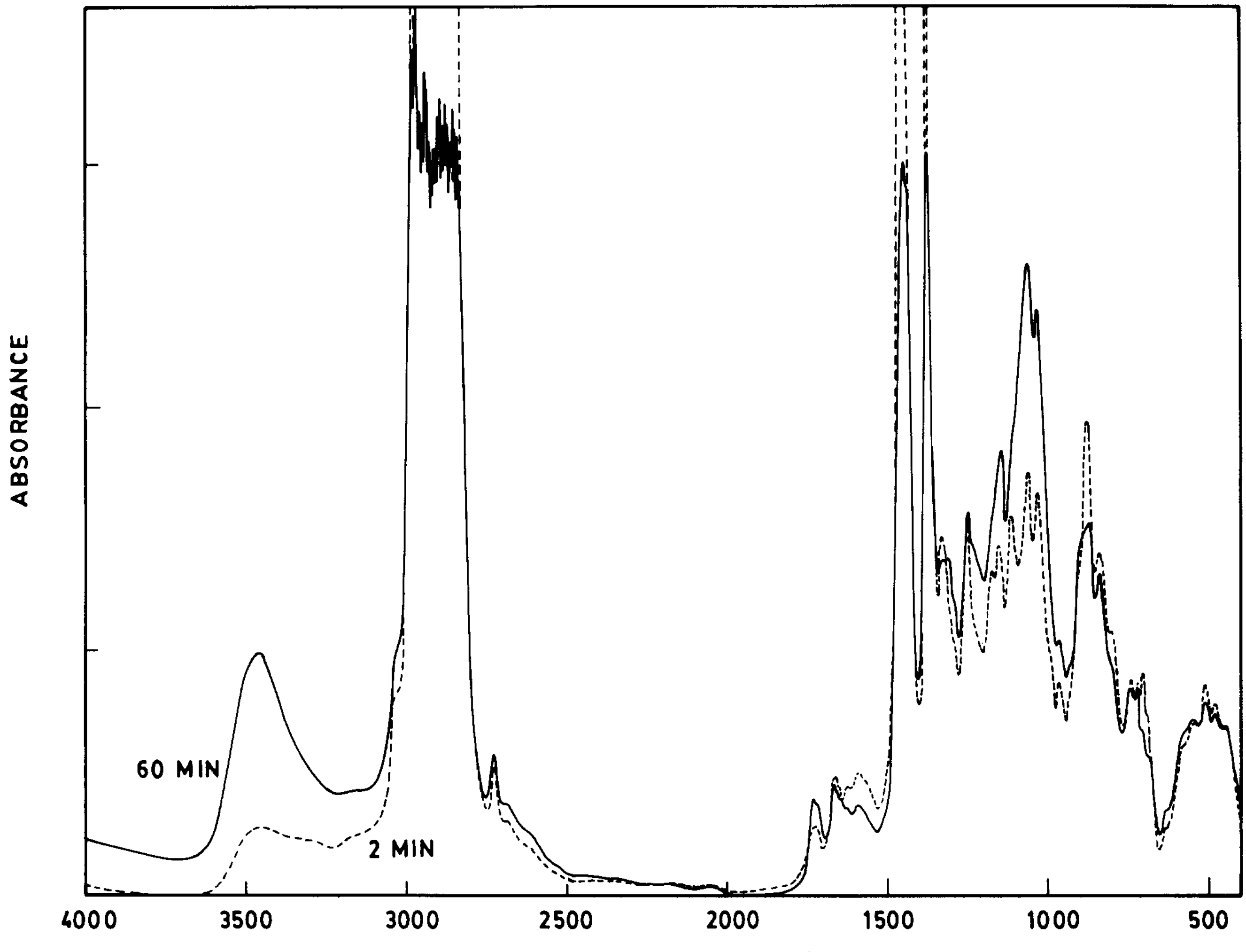


Figure 9 Infra-red spectra of the 50/50 sEPDM/ENR blends, moulded for 2 and 60 min

Table 3 Glass transition temperatures (°C) of the sEPDM/ENR blends as determined by d.s.c. and d.m.a. (data in parentheses refer to T_g during second heating)

Composition sEPDM/ENR	Moulding time, at 170°C (min)	D.s.c.		Dynamic mechanical studies: Tan δ peak position		Dynamic mechanical studies: Loss modulus peak position	
		a	*b*	*a*	*b*	*a*	*b*
100/0	2	−55(−55)	-	−45	-	−53	-
75/25	2	−53.5	−14	−47	−9,99	−53	−13
	60	−53.5	−1	−47	+18	−53	+14
50/50	2	−55(−55)	−16(+15)	−47	−9	−53	−13
	60	−55(−55)	−11.5(+12)	−47	−1	−53	−7
25/75	2	−53.5	−15	−49	−9	−53	−13
	60	−53.5	−15	−47	−9	−51	−13
0/100	2	-	−17(−16)	-	−1	-	−15

[a] Due to sEPDM
[b] Due to ENR

Table 4 Main i.r. vibrational bands of the 50/50 sEPDM/ENR blend

Peak (cm^{-1})	Assignment[a]	Change in absorbance after 60 min moulding
877	epoxy ring vibration	Decrease
1026 1065 1115	(i) polymer backbone vibration (ii) ν_{C-O-C}, ν_{C-O} (ethers) (iii) ν_{C-O} (furans) (iv) sym ν_{SO_3} (sulfonates)	Increase and broadening
1160	(i) $\nu_{C-O}+\delta_{O-H}$ (tert. alcohol) (ii) ν_{C-O} (furans) (iii) asym ν_{SO_3} (sulfonates)	Increase
1250	(i) ν_{C-O} (epoxy ring) (ii) CH_2 wagging motion	No change
1732	$\nu_{C=O}$ (ketones, acetates)	Increase
3250–3600	ν_{O-H} (intermolecular hydrogen bond)	Increase and broadening

[a] Refs 30 and 31

8 Lundberg, R. D. and Phillips, R. R. 'Coulombic Interactions in Macromolecular Systems', ACS Symp. Ser. 302, American Chemical Society, Washington, DC, 1986, Ch. 16
9 Xie, H. Q. and Ma, B. Y. 'Contemporary Topics in Polymer Science', vol. 6 (Ed. M. B. Culbertson), Plenum, New York, 1989
10 Xie, H. Q., Xu Jigeng and Zhou Shibias *Polymer* 1991, **32**, 95
11 Smith, P. and Eisenberg, A. *J. Polym. Sci., Polym. Lett. Edn.* 1983, **21**, 223
12 Bazuin, C. G. and Eisenberg, A. *J. Polym. Sci., Polym. Phys. Edn.* 1986, **24**, 1021
13 Lu, X. and Weiss, R. A. *Macromolecules* 1991, **24**, 4381
14 Alex, R., De, P. P., Mathew, N. M. and De, S. K. *Plast. Rubber Process. Appl.* 1990, **14**, 223
15 Alex, R., De, P. P. and De, S. K. *Kautsch. Gummi Kunst.* 1991, **44**, 333
16 Mukhopadhyay, S. and De, S. K. *Polymer* 1991, **32**, 1223
17 Mukhopadhyay, S., De, P. P. and De, S. K. *J. Appl. Polym. Sci.* 1991, **43**, 347
18 Ramesh, P. and De, S. K. *J. Mater. Sci.* 1991, **26**, 2846
19 Ramesh, P. and De, S. K. *Rubber Chem. Technol.* 1992, **65**, 24
20 Manoj, N. R., De, P. P. and De, S. K. *J. Appl. Polym. Sci.* in press
21 Gelling, I. R. *Rubber Chem. Technol.* 1985, **58**, 86
22 Agarwal, P. K., Makowski, H. S. and Lundberg, R. D. *Macromolecules* 1980, **13**, 1679
23 Tant, M. R. and Wilkes, G. L. *J. Macromol. Sci.-Rev. Macromol. Chem. Phys.* (*C*) 1988, **28**(1), 1
24 Davey, J. E. and Loadman, M. J. R. *Br. Polym. J.* 1984, **16**, 134
25 Baker, C. S. L., Gelling, I. R. and Newell, R. *Rubber Chem. Technol.* 1985, **58**, 67
26 Mauritz, K. A. *J. Macromol. Sci.-Rev. Macromol. Chem. Phys.* (*C*) 1988, **28**(1), 65
27 Treloar, L. R. G. 'The Physics of Rubber Elasticity', 2nd Edn., Oxford University Press, Oxford, 1958
28 Sakamoto, K., MacKnight, W. J. and Porter, R. S. *J. Polym. Sci.* (*A*) 1970, **2**(8), 277
29 Eisenberg, A. and Navratil, M. *Macromolecules* 1973, **6**, 604
30 Agarwal, P. K., Dutta, P. K. and Lundberg, R. D. *Polymer* 1987, **28**, 1467
31 Socrates, G., 'Infrared Characteristic Group Frequencies', Wiley, New York, 1980
32 Rosowski, A., 'Heterocyclic Compounds with Three and Four Membered Rings, Part 1', Interscience, New York, 1964
33 Loo, C. T., Proc. Int. Rubber Conf., Rubber Research Institute of Malaysia, Kuala Lumpur, 1985, p. 368
34 Gelling, I. R. and Morrison, N. J. *Rubber Chem. Technol.* 1985, **58**, 243
35 Parker, R. E. and Issacs, N. S. *Chem. Rev.* 1959, **59**, 737
36 Buchanen, J. G. and Sable, H. Z. 'Selective Organic Transformations' (Ed. B. S. Thyagarajan), Interscience, New York, 1972, Vol. 2