

# Self-Crosslinkable Blend of Zinc-Sulfonated EPDM and Epoxidized Natural Rubber\*

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## SYNOPSIS

The zinc-sulfonated EPDM (SEPDM)–epoxidized natural rubber (ENR) blend is self-crosslinkable in the sense that it undergoes crosslinking on molding at high temperatures without the aid of any external curing agents. This is evident from Monsanto rheometric, solvent swelling, and infrared spectroscopic studies. The sulfonate anion is believed to react with an epoxide ring, leading to the formation of sulfonate ester and ether crosslinks. The extent of crosslinking depends on the degree of sulfonation of SEPDM and epoxidation level of ENR, the blend ratio, molding time, and temperature. Dynamic mechanical analyses of the blends show the immiscibility of the blend components. The chemical interaction is also manifested in the shift of the glass transition temperature of ENR to the high-temperature region. © 1994 John Wiley & Sons, Inc.

## INTRODUCTION

Ionic polymers or ionomers form a group of polymers that have been receiving ever-increasing attention because of their unique properties, both in the solid state and solution, resulting from the pendant ionic groups that are usually neutralized by metals.<sup>1–4</sup> The resultant properties are dependent on the ionic content, degree of neutralization, type of cation, and the distribution of ionic groups in the polymer. These materials are assumed to be heterogeneous as the ionic groups segregate into multiplets, aggregates, clusters, and inverted micelles, instead of being uniformly distributed.<sup>5</sup> Polymers containing sulfonate groups neutralized by metal counterions, especially sulfonated ethylene propylene diene rubber (SEPDM) and sulfonated polystyrene (SPS), have gained special interest because of their unique properties arising from stronger ionic interactions as compared to other ionic groups.<sup>2</sup> Both SEPDM

and SPS show marked ionic aggregation even at low levels of sulfonation.<sup>6</sup> However, this ionic reticulation produced by the neutralization is reversible on heating and shearing.<sup>2,4</sup> This reversibility allows the viscosity of ionomers to be decreased down to such a level that these materials can be easily processed.<sup>2,4</sup>

Ionomers produce interesting blend systems with other polymers. Blends of SEPDM with polypropylene, polyethylene, poly(vinyl chloride), poly(ethylene oxide), and sulfonated butyl rubber exhibit some unique properties.<sup>7,8</sup> Ionic interactions in the blend components improve compatibility.<sup>9</sup> Successful examples are the blends of SPS and poly(ethyl acrylate-co-4-vinyl pyridine),<sup>10</sup> and SPS and polyamide-6.<sup>11</sup> The different types of specific interactions used in the ionomer blends include acid-base,<sup>12</sup> ion-dipole,<sup>13</sup> and transition metal complexation.<sup>14</sup>

Blends of polymers containing appropriate chemical groups that can interact at high temperature to form chemical crosslinks without the aid of any external curing agents have been termed “self-crosslinkable polymer blends”.<sup>15–19</sup> Examples of such novel blends are carboxylated nitrile rubber (XNBR)–epoxidized natural rubber (ENR),<sup>15</sup> chlorosulfonated polyethylene–XNBR,<sup>16</sup> poly(vinyl chloride) (PVC)–ENR,<sup>17</sup> PVC–NBR,<sup>18</sup> PVC–

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**Table I Summary of Monsanto Rheometric Studies**

Blend	Composition	Test Temperature (°C)	Minimum Torque (dN.m)	Rheometer Scorch Time <sup>a</sup> (min)	Torque after 120 min (dN.m)
SEPDM25-ENR50	0/100	170	1	—	2
	25/75	170	1	6	24
	50/50	150	5	30	10
		170	4	8	40
		190	4	6	48
		170	9	4	57
100/0	170	42	—	39	
SEPDM25-ENR25	0/100	170	1	—	1
	25/75	170	1	110	3
	50/50	170	6	11	36
	75/25	170	8	8	47
	100/0	170	42	—	39
SEPDM10-ENR50	0/100	170	1	—	2
	25/75	170	3	—	3
	50/50	170	4	30	18
	75/25	170	8	8	35
	100/0	170	28	—	25
SEPDM10-ENR25	50/50	170	1	—	1
SEPDM25-NR	50/50	170	3	—	3
EPDM-ENR50	50/50	170	1	—	1

<sup>a</sup> Time for a 2-unit torque rise beyond the minimum torque.

HNBR,<sup>19</sup> and chlorinated rubber-XNBR.<sup>20</sup> The chemical interaction is expected to be taking place through condensation and substitution reactions. Ionomers are likely to play an interesting role in such chemically interacting systems.

This study reports the results of the studies on the blend of zinc salt of sulfonated EPDM (SEPDM) and epoxidized natural rubber (ENR), with special reference to the effect of variation of sulfonation level and epoxy content of the constituent rubbers on the blend properties.

## EXPERIMENTAL

### Materials

The SEPDM (obtained from Exxon Research and Engineering Company, New Jersey, U.S.A.) consists of 50% ethylene and 5% 5-ethylidene-2-norbornene. The sulfonation level was 10 and 25 meq/100 g polymer. They will be designated hereafter as SEPDM10 and SEPDM25, respectively. The Mooney viscosity values [ML(1 + 4), 100°C] were 16 and 20, respectively. The ENR was procured from Kumpulan Gutheric Berhad, Malaysia. The epoxy-

ation level was 25 mol % (ENR25) and 50 mol % (ENR50). The ML(1 + 4) values at 100°C were 27 and 44, respectively.

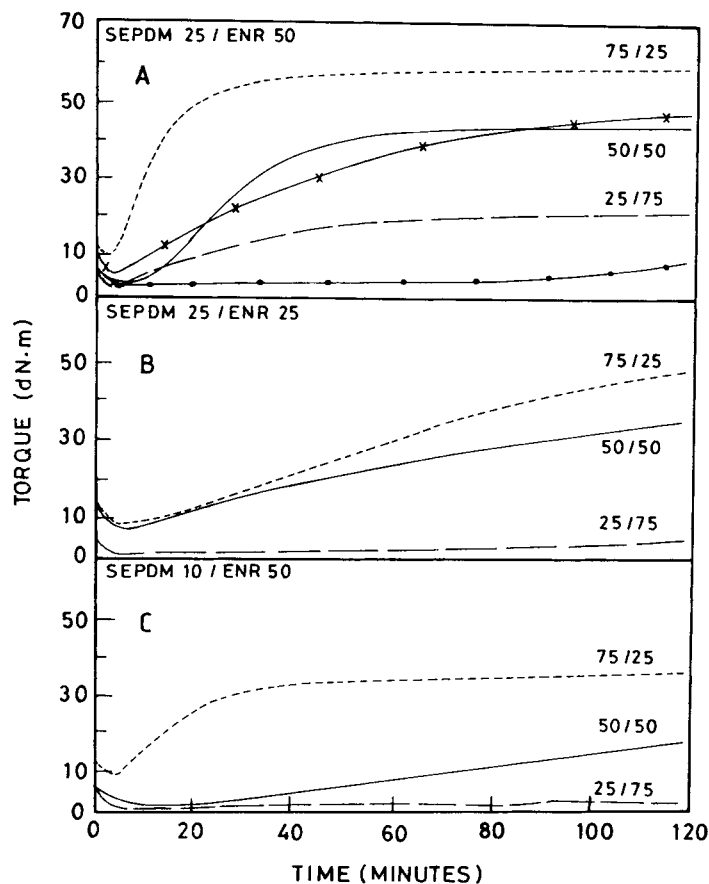
### Blend Preparation

The blends, according to the formulations in Table I, were prepared in a tight-nipped two-roll mill. First, ENR was masticated for 2 min and then the SEPDM was added. Total mixing time was 7 min. The mixing temperature was maintained around 30°C by water circulation.

### Blend Characterization

Monsanto rheographs of the different blends were obtained in a Monsanto Rheometer R100. The blends were molded in a hydraulic press at 170°C.

The dynamic mechanical analyses of the samples (20 × 5 × 2 mm) were performed in a Rheovibron DDV III-EP dynamic viscoelastometer under extension-compression mode at a frequency of 3.5 Hz. Experiments were done 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.



**Figure 1** Rheographs: (a) (----) 25/75 SEPDM25-ENR50, (-----) 75/25 SEPDM25-ENR50 at 170°C; 50/50 SEPDM25-ENR50 at (—●—●—●—●—) 150°C; (—) 170°C; and (×××××) 190°C. (b) SEPDM25-ENR25 blends at 170°C: (----) 25/75, (—) 50/50, and (-----) 75/25. (c) SEPDM10-ENR50 blends at 170°C: (----) 25/75, (—) 50/50, and (-----) 75/25.

The infrared (IR) spectra of the thin films of the samples (molded at 170°C) were obtained with a Bruker IFS-66 FTIR instrument, by mounting an ATR attachment. The internal reflection element used was 45° KRS-5. Five hundred scans of 4 cm<sup>-1</sup> resolution were signal averaged in each case.

## RESULTS AND DISCUSSION

### Rheometric Studies

Monsanto rheographs of the blends at different blend ratios and temperatures are shown in Figure 1. The progressive formation of a crosslinked network in the system is manifested in the gradual rise in the torque with curing time. There is no increase in torque with time when either the sulfonate or epoxy groups are absent in the polymer backbone,

as seen in the blends of SEPDM-natural rubber and EPDM-ENR (Table I). Since the neat polymers (SEPDM or ENR) do not show any torque rise, the possibility of thermovulcanization of the component polymers in the blend is also eliminated. This indicates that the chemical interaction takes place between the functional groups in the two rubbers, namely SEPDM and ENR. As the curing temperature increases from 150 to 190°C, the rate and extent of crosslinking reaction also increases, as shown in Figure 1 for the 50/50 SEPDM25-ENR50 blends. At 150°C, there is only a 5-unit rise in the torque, whereas at 190°C the blend registers a 42-unit rise in a span of 2 h. Table I summarizes the results of all the blends and the single components, indicating the minimum torque, torque after 120 min, and the time for 2 units torque rise (scorch time).

On the basis of maximum torque values of the 50/50 blends of the four different systems, it is ap-

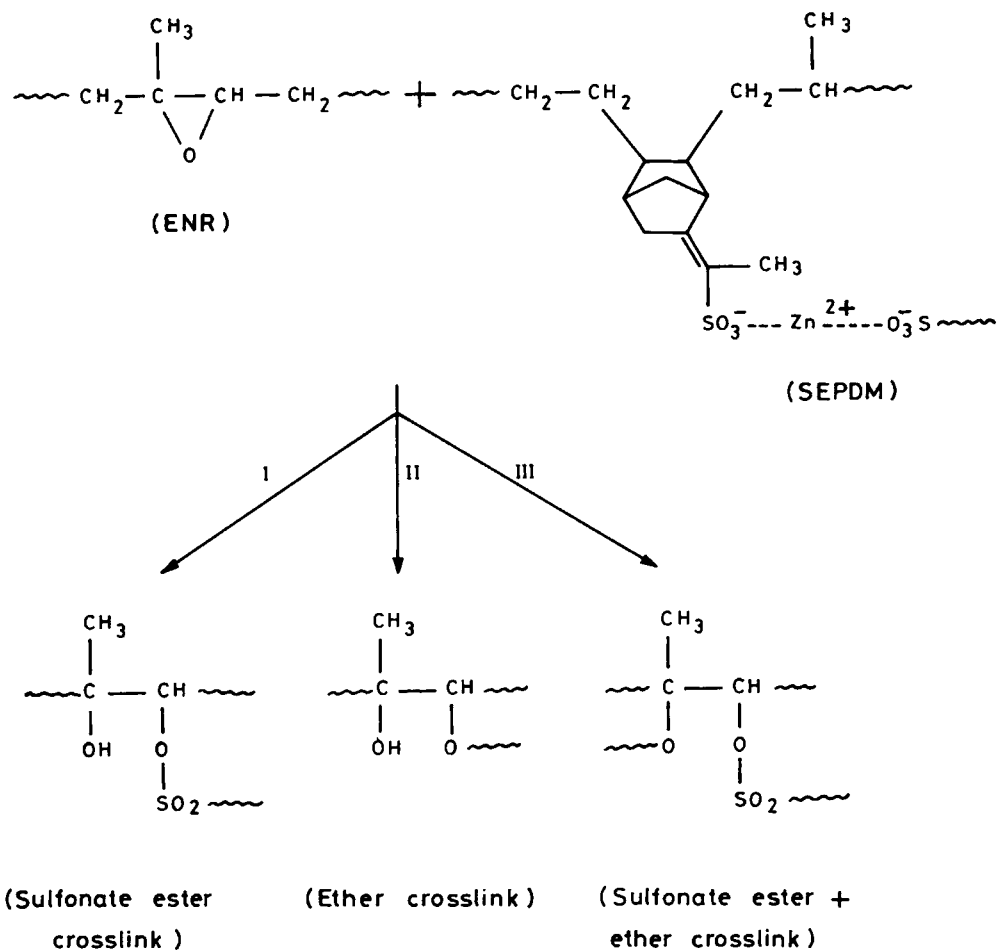


Figure 2 Proposed mechanism of crosslinking in SEPDM-ENR blends.

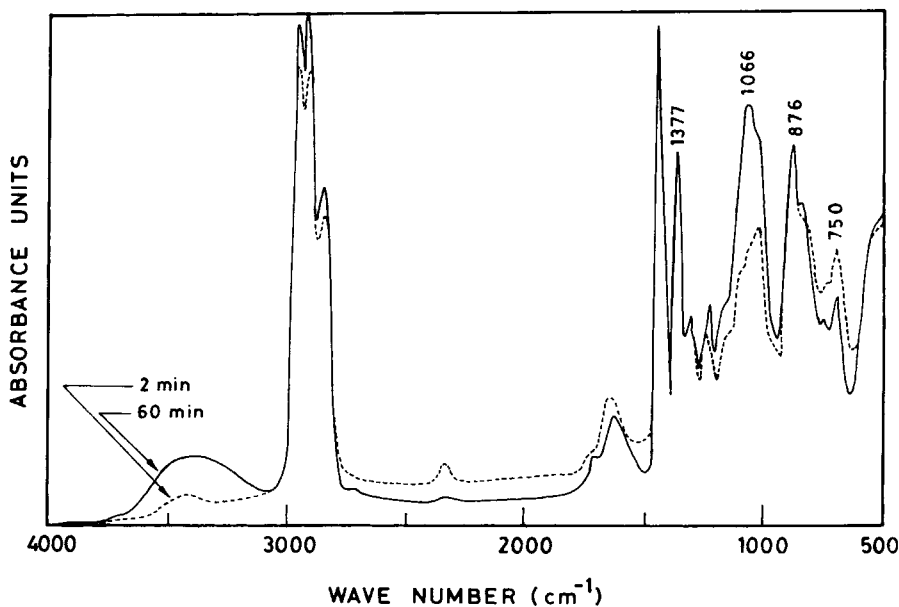
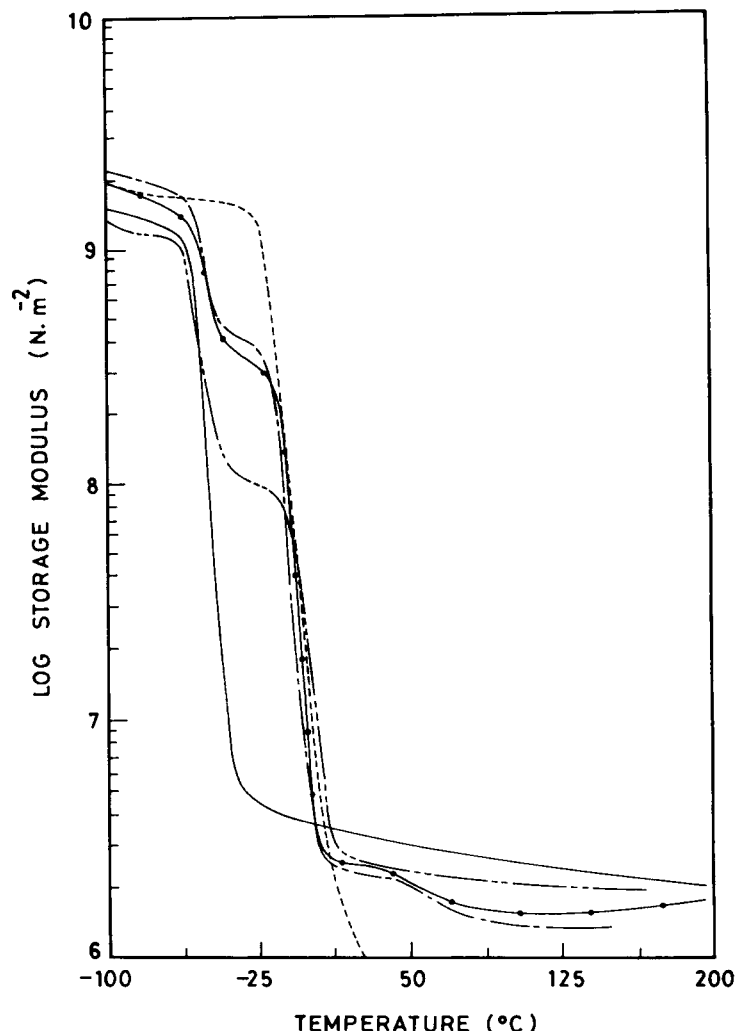


Figure 3 Infrared spectra of SEPDM25-ENR50 blends molded for 2 min (-----) 2 min and (—) 60 min at 170°C.



**Figure 4** Plot of storage modulus vs. temperature of (—) SEPDM10, (-----) ENR50; 50/50 SEPDM10-ENR50 blends molded for 2 min (-----) 2 min and (- · - · - ·) 60 min; and 75/25 SEPDM10-ENR50 blend molded for (-----) 60 min.

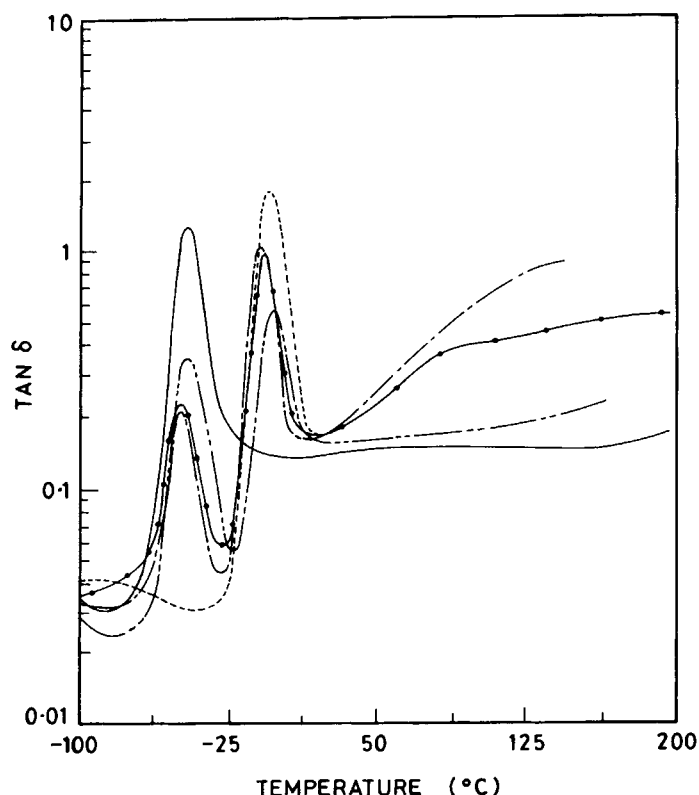
parent that the degree of crosslinking follows the order SEPDM25-ENR50 > SEPDM25-ENR25 > SEPDM10-ENR50 > SEPDM10-ENR25. The 75/25 SEPDM-ENR blends register the highest degree of crosslinking as compared to the 50/50 or 25/75 blends in each case. The 50/50 SEPDM10-ENR25 blend shows no torque rise and the case with the 25/75 SEPDM25-ENR25 and SEPDM10-ENR50 blends is similar, which may be attributed to the low concentration of the functional groups.

#### Swelling Studies

Further evidence for the SEPDM-ENR crosslinking during molding is provided by the solvent swelling

studies. The neat rubbers, as well as the blends before molding, are soluble when kept immersed in a solvent mixture of 50/10/40 *n*-heptane-ethanol-tetrahydrofuran at 30°C for 48 h. However, the 50/50 and 75/25 SEPDM25-ENR50 blends, molded for 60 min, swell only to a limited extent (percent increase in volume, 345 and 215, respectively). The 25/75 blend, however, dissolved even after molding, which shows a very low degree of crosslinking. The results are thus consistent with the rheometric studies.

In the case of SEPDM10-ENR50 blends, the 50/50 and 75/25 blends, molded for 60 min, swell to a limited extent (percent increase in volume, 675 and 295, respectively), while the 25/75 blend dissolves



**Figure 5** Plot of loss tangent vs. temperature of SEPDM10-ENR50 blends (legends same as in Fig. 4).

completely. However, the blends of SEPDM25-ENR25 were soluble, except the 75/25 blend, which was molded for 60 min (percent increase in volume, 960). This observation is different from the results of the rheometric studies where SEPDM25-ENR25 blends show higher torque rise than for the SEPDM10-ENR50 blend. The discrepancy may be attributed to the intramolecular chemical rearrangements (especially furanization) in ENR, the rate of which will be higher in ENR50.<sup>21</sup> Hence, though the crosslinking reaction may be higher in SEPDM25-ENR25, the SEPDM10-ENR50 blend swells less. The same trend is manifested in the dynamic mechanical analysis also.

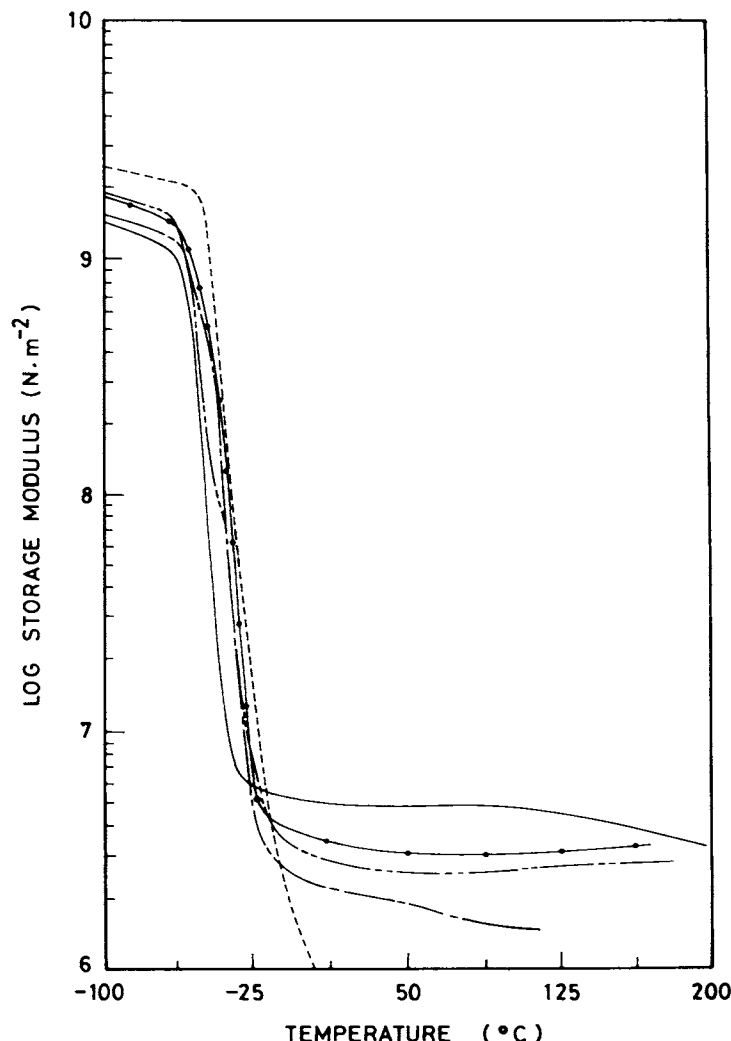
#### Mechanism of Crosslinking and IR Studies

The stability of the epoxide ring is controlled both by electronic and steric factors.<sup>22</sup> Mineral acids have a marked catalytic effect on epoxide cleavage. Carboxylic acids attack epoxides to produce monoesters of 1,2-diols.<sup>23</sup> The ring opening reaction of ENR by XNBR, resulting in ester linkages, has been re-

ported.<sup>15</sup> Sulfonic acids, being stronger than the carboxylic acids, are expected to interact strongly with ENR. It has been reported that sulfenic acids and sulfoxides cause ring opening of epoxides.<sup>21</sup> Based on these observations, a probable reaction pathway for the chemical interaction between SEPDM and ENR is shown in Figure 2.

The sulfonate anion, being a good nucleophile, attacks the carbon bearing the epoxide group in accordance with the Markownikoff's rule, effecting ring opening. Among the easiest epoxide reactions to occur are those in which a nucleophile attack on the carbon is followed by complexing of the epoxy oxygen by an electrophilic center in the same or a different molecule.<sup>24</sup> Hence the sulfonate anion attack leads to the formation of ester and ether linkages as shown in Figure 2. Secondary side products include diols and furans (cyclic ethers) formed in ENR when there are two adjacent epoxide groups.<sup>21</sup>

Infrared spectroscopic analysis provides evidence to the formation of new linkages (Fig. 3). The two spectra correspond to the 50/50 SEPDM25-ENR50 blends, molded for 2 and 60 min. The characteristic



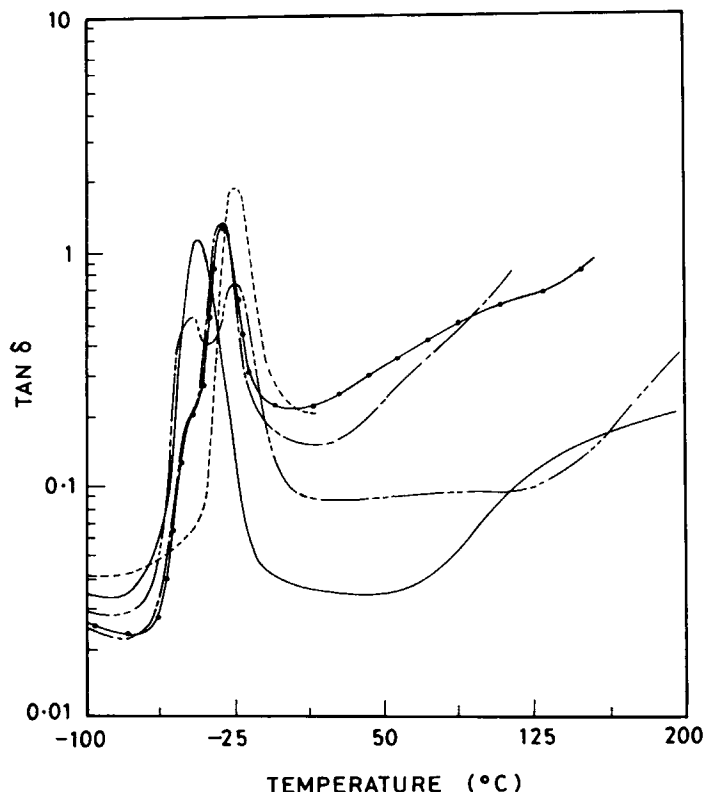
**Figure 6** Plot of storage modulus vs. temperature of (—) SEPDM25, (-----) ENR25; 50/50 SEPDM25-ENR25 blend molded for (-----) 2 min and (.....) 60 min; and 75/25 SEPDM25-ENR25 blend molded for (-·-·-·-) 60 min.

peaks of SEPDM appear at 1065, 1115, and 1160  $\text{cm}^{-1}$  due to the symmetric stretching of the sulfonate group,  $-\text{CH}_2$  motions of the polymer backbone, and the asymmetric stretching of the sulfonate group, respectively.<sup>25</sup> Epoxides absorb near 1250 and 750  $\text{cm}^{-1}$  due to the C—O stretching and ring vibrations, respectively.<sup>26</sup> The reduction in the absorbance at 750  $\text{cm}^{-1}$  points to the decrease in the epoxy ring concentration due to the ring opening reactions. The 1250  $\text{cm}^{-1}$  peak is not affected because furans (which are formed as side products) also absorb in this region. The broadening and increased absorbance at 3250–3600  $\text{cm}^{-1}$  correspond to the formation of hydroxyl groups in the system. The increase in the absorbance at 1020–1160  $\text{cm}^{-1}$  region can be

attributed to the formation of ether crosslinks. The sulfonate ester groups absorb in the same region as the sulfonate groups.

#### Dynamic Mechanical Analysis

Figures 4–7 show typical plots of storage modulus ( $E'$ ) and loss tangent ( $\tan \delta$ ) against temperature of the blends of SEPDM10-ENR50 and SEPDM25-ENR25, and the single polymers. The viscoelastic behavior of SEPDM<sup>27,28</sup> and ENR<sup>29,30</sup> has been studied earlier. The most striking feature regarding the mechanical behavior of SEPDM, as seen from the storage modulus vs. temperature plots, is the presence of the rubbery plateau that extends up to



**Figure 7** Plot of loss tangent vs. temperature of SEPDM25-ENR25 blends (legends same as in Fig. 6).

200°C, unlike ENR, which shows viscous flow above its glass transition temperature ( $T_g$ ). This broadened rubbery plateau in the case of SEPDM is due to the presence of ionic aggregates that provide a temperature-resistant network in the form of ionic multiplets and clusters that result from ion-pair interaction.<sup>28</sup> The transition at  $-45^\circ\text{C}$  corresponds to the relaxation of the ion-free backbone.

The dynamic mechanical analyses further demonstrate the immiscibility of the blend components since they exhibit two transitions, corresponding to the individual rubbers (Figs. 4 and 5). The blends of SEPDM25-ENR25 show a single transition with a shoulder, due to the close proximity of the two transitions (Figs. 6 and 7). The immiscibility arises presumably due to the fact that the nonpolar or nonionic parts comprise the major constituent of the blend, which are not involved in the chemical interaction. The results are summarized in the Table II.

The blends molded for 2 min show a downward shift in the ENR transitions peak (from  $-1$  to  $-7^\circ\text{C}$ ), reasons for which are not clear at the moment. However, on molding for 60 min, the ENR peak shifts to the high-temperature side. This shift

is the highest in the case of the SEPDM25-ENR50 blends, which have shown the highest extent of reaction, as rated from the Monsanto rheometric and solvent swelling studies. Similarly, in each case, the 75/25 SEPDM-ENR blends show the greatest extent of reaction as compared to the 50/50 or 25/75 blends. This change in the  $T_g$  can be ascribed to the structural changes taking place in ENR during the crosslinking reaction.<sup>21</sup> Phase inhomogeneity due to ring-opened products in ENR is readily observable in the broadening and shifting of its  $T_g$ .<sup>30</sup> In the case of the SEPDM10-ENR50, only the 75/25 blend shows some shift, and the SEPDM25-ENR25 blends do not show any shift. This is because when the degree of sulfonation and epoxidation is low, the rate of reaction and hence the extent of structural changes in ENR is less.

### Physical Properties

The physical properties of the different blends are summarized in Table III. The blends, on crosslinking, exhibit higher tensile strength and elongation at break. The tear resistance also is improved upon



**Table II Glass Transition Temperatures of SEPDM–ENR Blends as Determined from Dynamic Mechanical Analysis**

Blend	Composition	Molding Time (at 170°C) (min)	Tan $\delta$ Peak Position (°C)	
			SEPDM	ENR
SEPDM25–ENR50	100/0	2	-45	—
	25/75	2	-48	-7
	25/75	60	-48	-7
	50/50	2	-48	-9
	50/50	60	-48	-1
	75/25	2	-48	-9
	75/25	60	-47	+18
SEPDM10–ENR50	0/100	2	—	-1
	100/0	2	-45	—
	25/75	2	-47	-7
	25/75	60	-47	-7
	50/50	2	-47	-7
	50/50	60	-47	-7
	75/25	2	-47	-7
SEPDM25–ENR25	75/25	60	-47	+1
	0/100	2	—	-1
	100/0	2	-45	—
	25/75	2	-47	-31
	25/75	60	-47	-31
	50/50	2	-47	-31
	50/50	60	-47	-31
SEPDM25–ENR25	75/25	2	-47	-31
	75/25	60	-47	-31
	0/100	2	—	-27

**Table III Physical Properties of the Blends**

Blend	Molding Time (min)	Tensile Strength (MPa)	Elongation at Break (%)	Tear Strength (kN/m)	Hardness (Shore A)	Resilience (at 50°C) (%)
SEPDM25–ENR50						
0/100	2	0.5	335	3.8	17	23
25/75	2	0.3	667	3.3	25	27
25/75	60	0.3	1211	2.0	25	22
50/50	2	0.6	208	4.5	25	20
50/50	60	3.1	427	12.6	52	23
75/25	2	0.9	169	6.9	45	29
75/25	60	7.8	450	29.2	59	27
100/0	2	8.4	474	33.3	57	27
SEPDM10–ENR50						
0/100	2	0.5	335	3.8	17	23
25/75	60	0.3	2154	3.3	26	23
50/50	2	0.4	661	6.2	32	18
50/50	60	1.9	1084	13.5	45	27
75/25	60	4.1	870	25.1	53	32
100/0	2	1.3	224	16.2	45	28
SEPDM25–ENR25						
0/100	2	0.4	370	4.6	22	29
25/75	60	0.3	1055	2.2	24	16
50/50	2	0.4	146	3.7	25	20
50/50	60	0.5	155	4.1	30	20
75/25	60	2.1	260	16.1	50	27
100/0	2	8.4	474	33.3	57	27

molding. Resilience is not greatly affected, but hardness increases with crosslinking.

## CONCLUSIONS

That the blend of SEPDM and ENR is self-cross-linkable during high-temperature molding is evident from the Monsanto rheometric, solvent swelling, and IR studies. The extent of crosslinking depends on the blend ratio, degree of sulfonation of SEPDM, level of epoxidation of ENR, and the molding conditions. The chemical interaction is believed to take place through the nucleophilic attack on the epoxide ring by the sulfonate anion resulting in sulfonate ester and ether linkages. Dynamic mechanical analyses show the immiscibility of the blend components. The ENR glass transition peak shifts to the higher temperature side on molding due to the structural changes taking place in ENR during the crosslinking reaction. Physical properties show improvement upon crosslinking.

## REFERENCES

1. A. Eisenberg and M. King, *Ion-Containing Polymers*, Academic Press, New York, 1977.
2. A. Eisenberg, *Ions in Polymers*, Advances in Chemistry Series 187, Academic Press, Washington, D.C., 1980.
3. A. Eisenberg and F. E. Barley, Eds., *Coulombic Interactions in Macromolecular Systems*, ACS Symp. Ser. 302, American Chemical Society, Washington, D.C., 1986.
4. W. J. MacKnight and R. D. Lundberg, *Rubber Chem. Technol.*, **57**(3), 652 (1984).
5. K. A. Mauritz and A. J. Hopfinger, in *Modern Aspects of Electrochemistry*, J. O. M. Bockris, B. E. Conway, and R. E. White, Eds., Plenum, New York, 1982, No. 14, pp. 425.
6. J. J. Fitzgerald and R. A. Weiss, *J. Macromol. Sci. Rev., Macromol. Chem. Phys.*, **C28**(1), 99 (1988).
7. H. Q. Xie and B. Y. Ma, in *Contemporary Topics in Polymer Science*, Vol 16, M. B. Culbertson, Ed., Plenum, New York, 1989.
8. H. Q. Xie, J. Xu, and S. Zhou, *Polymer*, **32**, 95 (1991).
9. P. Smith, M. Hara, and A. Eisenberg, *Curr. Top. Polym. Sci.*, **2**, 255 (1987).
10. A. Eisenberg, P. Smith, and Z. L. Zhou, *Polym. Eng. Sci.*, **22**, 17 (1982).
11. X. Lu and R. A. Weiss, *Macromolecules*, **24**, 4381 (1991).
12. Z. L. Zhou and A. Eisenberg, *J. Polym. Sci., Polym. Lett.*, **21**, 223 (1983).
13. M. Hara and A. Eisenberg, *Macromolecules*, **17**, 1375 (1984).
14. A. Sen and R. A. Weiss, *Polym. Prepr.*, **28**(2), 20 (1987).
15. R. Alex, P. P. De, N. M. Mathew, and S. K. De, *Plast. Rubber Comp. Process Appl.*, **14**, 223 (1990).
16. S. Mukhopadhyay, P. P. De, and S. K. De, *J. Appl. Polym. Sci.*, **43**, 347 (1991).
17. P. Ramesh and S. K. De, *J. Mat. Sci.*, **26**, 2846 (1991).
18. N. R. Manoj, P. P. De, and S. K. De, *J. Appl. Polym. Sci.*, **49**, 133 (1993).
19. N. R. Manoj, P. P. De, and S. K. De, *Rubber Chem. Technol.*, **66**, 550 (1993).
20. P. Ramesh and S. K. De, *Rubber Chem. Technol.*, **65**, 24 (1992).
21. I. R. Gelling and M. J. Morrison, *Rubber Chem. Technol.*, **58**, 243 (1985).
22. R. E. Parker and N. S. Issac, *Chem. Rev.*, **59**, 737 (1959).
23. R. T. Loo, Proc. Int. Rub. Conf., Rubber Research Institute of Malaysia, Kuala Lumpur, 368 (1985).
24. J. G. Buchanan and H. Z. Sable, in *Selective Organic Transformations*, Vol. 2, B. S. Thyagarajan, Ed., Interscience, New York, 1972, p. 1.
25. P. K. Agarwal, P. K. Dutta, and R. D. Lundberg, *Polymer*, **28**, 1467 (1987).
26. G. Socrates, *Infrared Characteristic Group Frequencies*, Wiley-Interscience, New York, 1980.
27. M. R. Tant and G. L. Wilkes, *J. Macromol. Sci. Rev., Macromol. Chem. Phys.*, **C28**(1), 1 (1988).
28. P. K. Agarwal, H. S. Makowski, and R. D. Lundberg, *Macromolecules*, **13**, 1679 (1980).
29. I. R. Gelling, *Rubber Chem. Technol.*, **58**, 67 (1985).
30. J. E. Davey and M. J. R. Loadman, *Brit. Polym. J.*, **16**, 134 (1984).

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