Effect of Reinforcing Carbon Black Filler on Thermally Induced Crosslinking of Polyacrylic Acid–Epoxidized Natural Rubber Blend

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SYNOPSIS

That carbon black filler influences the thermally induced crosslinking between polyacrylic acid (PAA) and epoxidized natural rubber (ENR) is evident from Monsanto rheometric studies, dynamic mechanical analyses, and physical property measurements. Considerable shift in glass transition temperature, as well as broadening of the loss peak due to ENR, along with disappearance of the loss peak due to PAA, indicate that HAF carbon black, at 20 parts per 100 of total polymer, make the immiscible PAA/ENR blend behave as a compatible blend. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Mallick et al.[1] reported that blend of polyacrylic acid (PAA) and epoxidized natural rubber (ENR) become crosslinked during high temperature molding in the absence of any extraneous crosslinking agent. Preliminary studies revealed that reinforcing carbon black fillers influence the crosslinking between PAA and ENR. It has been demonstrated that reinforcing carbon black filler can influence the sulfur vulcanization of rubber.[2-4] Participation of carbon black filler in the vulcanization mechanism has also been reported.[5-7] This article reports the results of our studies of the effect of HAF carbon black filler on the crosslinking between PAA and ENR.

EXPERIMENTAL

Details of the materials used are shown in Table I.

Preparation of PAA/ENR blends

The PAA/ENR blend ratio of 50/50 was maintained in the unfilled and filled blends. In the case

of filled blends, the HAF filler was added at loadings of 5, 10, 15, 20, and 25 parts by weight per 100 parts of total polymer. Mixing was done at 180°C and at the rotor speed of 90 rpm. In the case of the unfilled blend, ENR was first masticated in a Brabender Plasticorder PLE–330 for 1 min, followed by blending with PAA for another 10 min. In case of the carbon black filled blends, three mixing sequence techniques were followed. In the first technique, ENR was first masticated for 1 min. Carbon black was then added and was mixed for another 4 min. Finally, PAA was added and the whole mix was blended for 10 min. In the second mixing sequence, PAA was first allowed to be sheared for 1 min, followed by mixing carbon black for 4 min. ENR was then added and the whole mix was blended for 10 min. In the third mixing sequence, ENR was first masticated for 1 min, followed by mixing PAA for another 10 min. Carbon black was then added and the whole mix was blended for 4 min. Total mixing time was maintained at 15 min for each mixing technique.

Monsanto rheographs of the mixes were taken at 190°C, at times up to 120 min, using the Moving Die Rheometer–2000 at 0.5° arc rotation.

Each mix was molded for 120 min at 190°C and at a pressure of 10 MPa in a hydraulic press. The molded samples were cooled to room temperature under pressure. Test pieces were cut from the molded sheets.
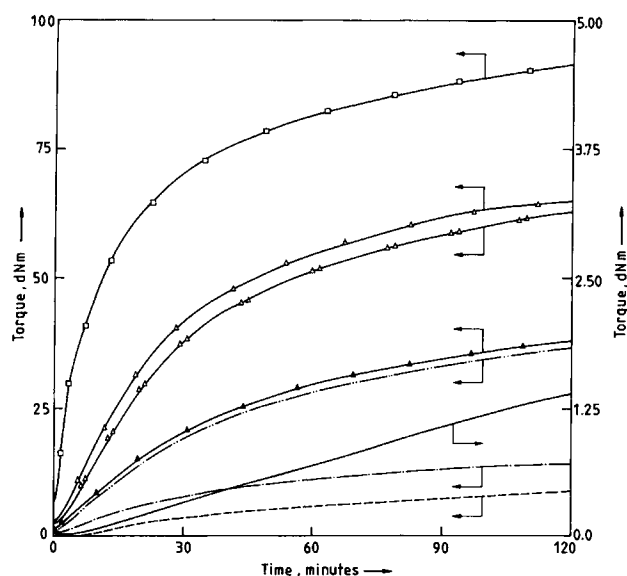
Figure 1 Effect of loadings of HAF carbon black filler and mixing sequence on Monsanto rheographs of 50/50 PAA/ENR blend. Rheographs were taken at 190°C. (a) Filler loading, (i) (———) 0 phr, (ii) (- - -) 5 phr, (iii) (- · - · -) 10 phr, (iv) (- · · - · · -) 15 phr, (v) (- Δ -) 20 phr, (vi) (- □ - □ -) 25 phr. Mixing done by first technique. (b) Mixing technique, (i) (- Δ -) first, (ii) (- Δ Δ -) second, (iii) (- ▲ -) third.

In order to study the effect of molding time on dynamic mechanical properties, the 20 phr HAF carbon black-filled mix was molded for 5, 30, 60, and 120 min at 190°C and at a pressure of 10 MPa.

Stress–strain properties were measured at room temperature (25 ± 2°C) using a Zwick Universal Tensile Testing Machine Model 1445, according to ASTM D 412-87, and ASTM D 624-86, respectively. The rate of separation of the grips was 500 mm/min.

Dynamic mechanical analyses of the samples (3 × 0.64 × 0.17 cm^3) were carried out using Rheovibron (Orientec Corporation, Japan) DDV–III–EP at a strain amplitude of 0.0025 cm and at a frequency of 3.5 Hz. The temperature rise was 2°C/min.

Table II Effect of Mixing Sequence on Physical Properties and Solvent Swelling of 20 phr HAF Carbon Black-Loaded PAA/ENR Blend[a]

| | Mixing Sequence | | |
Properties	First	Second	Third
25% Modulus (MPa)	7.00	6.82	5.50
50% Modulus (MPa)	—	8.81	7.25
Tensile strength (MPa)	10.52	9.68	7.50
Elongation at break (%)	52	63	56
Hysteresis loss (J/m^2) × 10^{-3}	28.3	26.1	20.1
Tear strength (N/mm)	29.6	28.2	20.1
Swelling studies:			
(i) Molded Sample:			
(i) Weight Loss[b] (%)	3	3	5
(ii) Nonmolded Sample:			
(i) Bound ENR[c] (%)	62	61	37
(i) Bound PAA[d] (%)	77	77	62

[a] Blends were molded for 120 min at 190°C.
[b] Samples were etched with chloroform for 168 h at 25 ± 2°C.
[c] Samples were etched with chloroform for 24 h at 25 ± 2°C.
[d] Samples were etched with methanol for 24 h at 25 ± 2°C.

The percent weight loss upon solvent swelling was calculated by taking the weight of the molded samples after having been swelled in chloroform (solvent for ENR) at 25 ± 2°C for 168 h. In another set of experiments, the nonmolded samples were allowed to swell in chloroform for 168 h at 25 ± 2°C. Swollen samples were dried at 100°C for 3 h and were weighed. A similar experiment was performed by swelling the samples in methanol (solvent for PAA). By taking the initial and final weights, the bound ENR and PAA were determined.

RESULTS AND DISCUSSION

Figure 1 shows the Monsanto rheographs of 20 phr HAF carbon black-filled PAA/ENR blends, mixed by three different techniques. In the first mixing se-
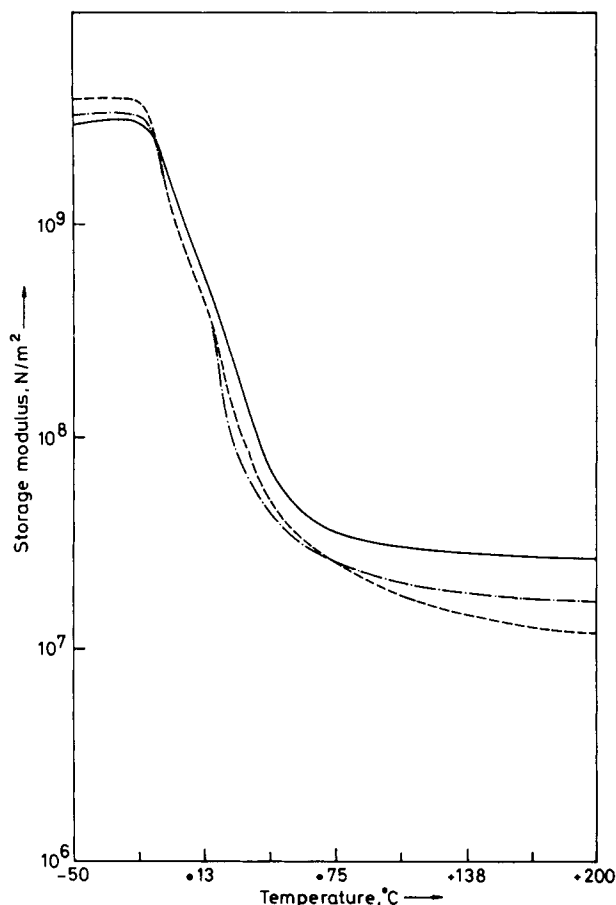
Table I Details of the Materials Used

Materials	Description	Source
Epoxyprene-50 (ENR)	$\bar{M}_n = 1,31,000$ $\bar{M}_w = 1,46,000$	Kumpulan Guthrie, Berhad, Malayasia
Polyacrylic Acid (PAA)	Copolymer of acrylic and methacrylic acids, average mol. weight range: 5,00,000–10,00,000	Fluka, Switzerland
Carbon Black	HAF (N-330); BET surface 62–88 m^2/g; average particle diameter 26–35 nm	Phillips Carbon Black Ltd., Durgapur, India

technique. The high temperature storage modulus values follow the following order: first technique > second technique > third technique.

Figure 3 shows the loss tangent vs. temperature plots of the blends. In the case of samples prepared by the second and third techniques, one single broad peak was observed around 16°C, but in the case of samples prepared by the first technique, apart from the broad peak, a secondary broad peak was observed around 20–26°C. The loss tangent peak height at the main transition zone, and in the high temperature region, follow this order: third technique > second technique > first technique. This shows that the degree of crosslinking follows the reverse order with the first technique registering the maximum extent of crosslinking. This is corroborated by the storage modulus results, as discussed earlier.

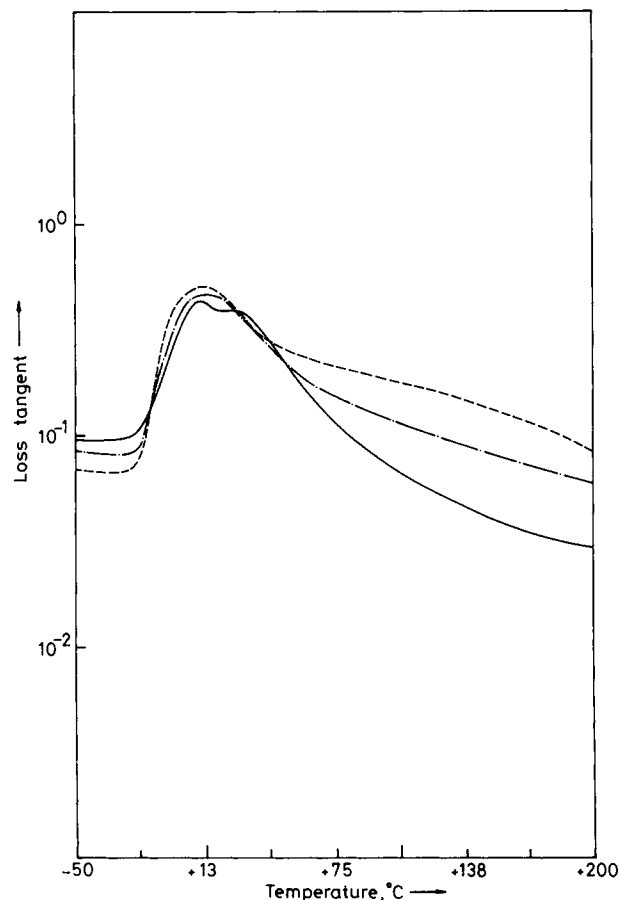The physical properties of the blends, prepared by the first and second techniques, are close to each

Figure 2 Effect of mixing sequence on the storage modulus vs. temperature plots of 20 phr HAF carbon black-filled 50/50 PAA/ENR blend, (i) (———) first, (ii) (– · – · –) second, (iii) (– – –) third. Blends were molded at 190°C for 120 min.

quence, ENR was premasticated and PAA was added last, and in the second mixing sequence, PAA was allowed to be sheared first and ENR was added last. In both cases, the rheometric torque rise was similar, but in the third mixing sequence, where carbon black was added in the last stage of mixing, the rheometric torque rise was much less than that of the first two techniques. This is believed to be due to poor dispersion of filler particles and to low polymer–filler interaction. This observation was further substantiated by dynamic mechanical analyses and physical property measurements (Table II).

Figure 2 shows the storage modulus vs. temperature plots of the blends, prepared by three mixing techniques. It is evident that the storage modului of the blends, mixed by the first and second mixing techniques, are comparable and much higher than that of the blend that was mixed by the third mixing

Figure 3 Effect of mixing sequence on the loss tangent vs. temperature plots of the 20 phr HAF carbon black-filled 50/50 PAA/ENR blend. Description of symbols same as in Figure 2. Blends were molded at 190°C for 120 min.
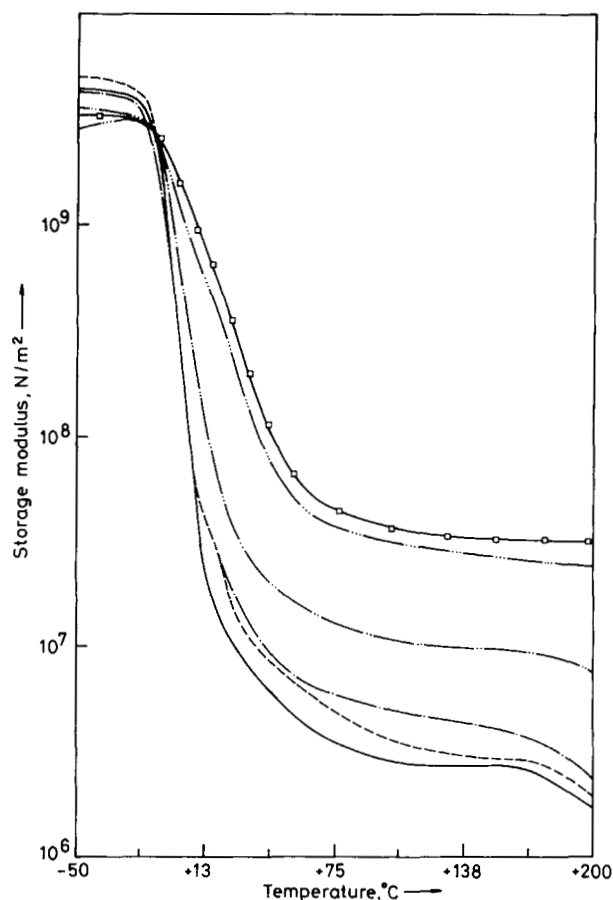
Figure 4 Effect of HAF carbon black filler loading on the storage modulus vs. temperature plots of the 50/50 PAA/ENR blend, (i) (———) 0 phr, (ii) (- - -) 5 phr, (iii) (- · - · -) 10 phr, (vi) (- · · - · · -) 15 phr, (v) (- · · · - · · · -) 20 phr, (vi) (-□-□-) 25 phr. Blends were mixed by the first technique and were molded at 190°C for 120 min.

other, while the same for the blend prepared by the third technique is far inferior. Swelling results indicate that the degree of crosslinking in the blend mixed by the third technique is much less than the blends prepared by the other two techniques. In view of the improved properties obtained for the blend prepared by the first technique, this first technique was used for subsequent studies on the effect of filler loading on the crosslinking and dynamic mechanical properties of the PAA/ENR blend.

Figure 1 shows the typical Monsanto rheographs of the PAA/ENR blends at various filler loadings. It is evident that, with an increase in filler loading, the rate of torque rise increases sharply. Moreover, it is noted that, in the presence of HAF carbon black filler, the torque rise becomes constant within 90 min. For the unfilled blend, however, the torque rise

continues even beyond 120 min. It is known that the incorporation of reinforcing filler increases both the rate and state of cure.[8-11]

Figure 4 shows the storage modulus vs. temperature plots of the PAA/ENR blend, containing different loadings of HAF carbon black filler. It is apparent that at low filler loading (up to 10 phr), two transitions, as in the case of the unfilled blend, could be detected. At high filler loading, however (20 phr and above), the second transition in the high temperature region was not observed and only one transition was observed. It is also noted that storage modulus increases with an increase in filler content and this increment is sharp at 20 phr filler loading. An increase in storage modulus, with the increase in filler loading, has been assigned to the increase in reinforcement.[12-15] In the case of crosslinked polymers, an increased degree of crosslinking is known to increase the storage modulus values.[16-17]
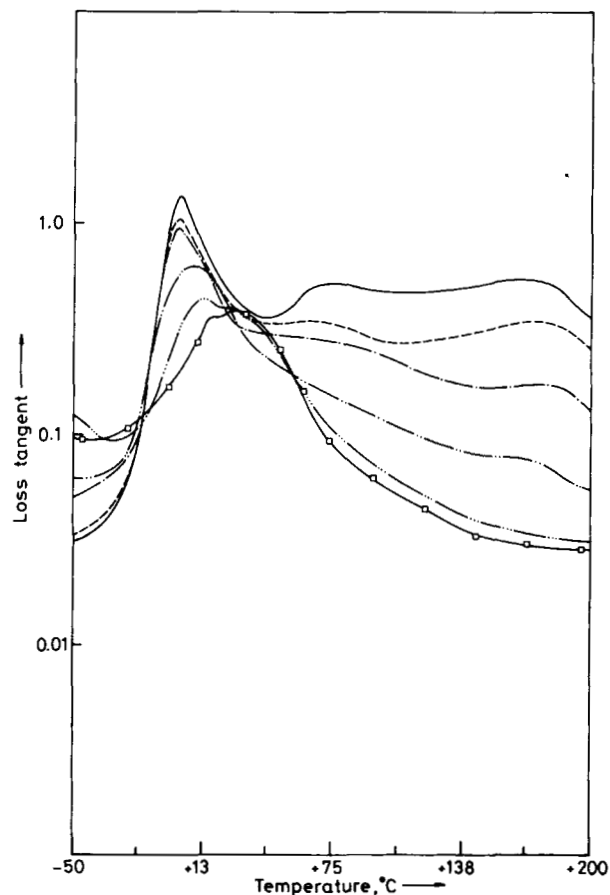

Figure 5 Effect of HAF carbon black filler loading on the loss tangent vs. temperature plots of the 50/50 PAA/ENR blend. Description of symbols same as in Figure 4. Blends were mixed by the first technique and were molded at 190°C for 120 min.
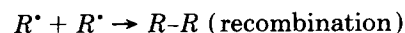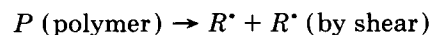
Table III   Glass Transition Temperatures and the Tanδ_{max} Values at ENR Transition Temperature for PAA/ENR Blends at Various Filler Loadings

Blend Designation PAA/ENR/HAF-Black	Glass Transition Temperature (°C)		Tanδ_{max} Value at ENR Transition Temperature
	Due to ENR	Due to PAA	
50/50/0	−1.2	159–164[a]	1.319
50/50/5	0.8	167–173[a]	1.067
50/50/10	0.8	167–171[a]	0.918
50/50/15	6.7	[b]	0.639
50/50/20	18.7–26.7[a]	[c]	0.416
50/50/25	20.0–28.6[a]	[c]	0.392

[a] Broad transition.
[b] No sharp transition.
[c] No transition.

Figure 5 shows the loss tangent vs. the temperature plots of the PAA/ENR blend, containing different loadings of filler. It is evident that at low filler loading (up to 10 phr), three peaks are observable: one peak around 2°C, due to the α-transition of ENR,[18–19] and two broad peaks around 50°C and 170°C, due to the β-and α-transitions of PAA.[20–21] Accordingly, the blend components can be described as immiscible.[22–24] At high filler loadings, however, the blends show three characteristic features in the loss tangent vs. temperature plots: (a) a sharp decrease in the loss peak due to ENR, which may be attributed to the increase in crosslink density and enhanced polymer–filler interaction at high filler content,[25–26] (b) considerable shift of glass transition temperature of the ENR phase by 30°C (Table III), which may be ascribed to the formation of a thick, immobilized layer surrounding the filler particles,[27–28] and (c) increased broadness of the α-transition peak, due to ENR along with disappearance of the high temperature loss peaks due to PAA, which indicates compatibility of the blend components.[22–24] In other words, at high loading, carbon black particles can cause a reduction in the heterogeneity of otherwise immiscible phases of the PAA/ENR blend.

Accordingly, it can be deduced that strong chemical and physicochemical interactions take place between the blend components and the filler particles, which led to reinforcement of elastomers by filler particles, as has been described by several authors,[29–33] and compatibility of the blend components. It has been reported earlier that chemical interaction between polymer and filler can take place during shearing through the following mechanism[30,34–35]:

$$P \,(\text{polymer}) \rightarrow R^{\cdot} + R^{\cdot} \,(\text{by shear})$$

$$R^{\cdot} + R^{\cdot} \rightarrow R\text{-}R \,(\text{recombination})$$

$$2\,R^{\cdot} + F \,(\text{filler}) \rightarrow RFR$$

(chemisorption of free radicals)

In the present case, three situations may arise: (a) filler particles, surrounded by PAA only (P-F in Fig. 9), (b) filler particles, surrounded by both PAA and ENR (P-F-E in Fig. 9), and (c) filler particles, surrounded by ENR only (E-F in Fig. 9).

It is believed that PAA, due to its high concentration of polar —COOH groups, is preferentially adsorbed onto the surface of the filler particles. Accordingly, the number of particles, represented as P-F, is larger than the number of particles represented as P-F-E, which is again larger than that represented as E-F. This is substantiated by the swelling data (Table IV), which shows that with the increase in filler content, bound PAA increases marginally, indicating little dependence of bound PAA on available active sites of filler. In addition, the high value of bound PAA indicates a strong interaction between the filler particles and PAA. It is also evident from Table IV that bound ENR depends on filler loading and it increases with an increase in filler content, since the available active sites for a fixed polymer content increase with the increase in filler loading.

Figure 6 compares the plot of the ratio of loss peak due to ENR for the filled blend, $(\tan\delta_{max})_f$, with that of the unfilled blend, $(\tan\delta_{max})_o$, vs. the volume fraction of filler. The plot is linear and follows an equation of this type:
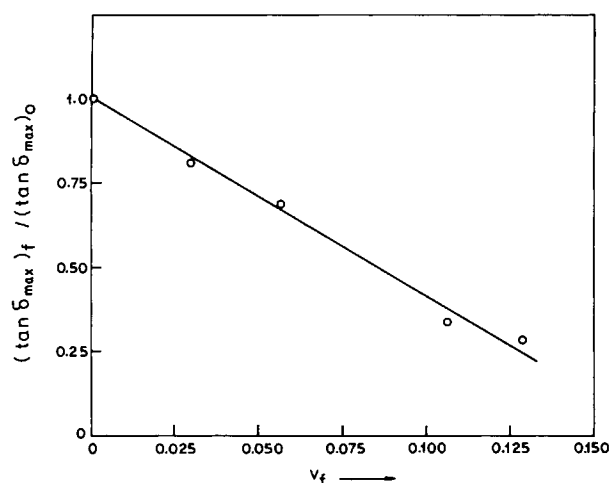
Figure 6 Plots of the ratio of loss peak values vs. volume fraction of filler; $(\tan\delta_{max})_f$, loss peak value for the filled system, and $(\tan\delta_{max})_o$, loss peak value for the unfilled system.

$$\frac{(\tan\delta_{max})_f}{(\tan\delta_{max})_o} = 1 - Bv_f \qquad (1)$$

where v_f is the volume fraction of filler and B is termed polymer–filler interaction parameter.[36] According to Neilson,[37] B is equal to 1, when there is no interaction between the polymer and the filler. In the present case, the value of B was 6.4, suggesting strong polymer–filler interaction. Similar values of

B have been reported in both plastic and rubber systems.[28,34]

Table IV also shows that hysteresis loss increases sharply with the increase in filler content, which has been assigned to the physical adsorption of elastomer chains that are surrounding the filler particles.[29,38-40] This is further substantiated by studying the effect of molding time on the 20 phr HAF carbon black filled blend, discussed below.

Figure 7 shows the effect of molding time on storage modulus vs. temperature plots of the blend, filled with 20 phr HAF carbon black. At low molding time, two transitions, one due to the ENR phase and another due to the PAA phase, are observable. An increase in molding time causes the high temperature transition, due to PAA phase, to disappear. A similar observation was made while studying the effect of molding time on loss tangent vs. temperature plots of the blend mentioned above (Fig. 8). Two broad peaks, due to PAA, disappear gradually along with the broadening and shifting of the low temperature loss peak, due to ENR, to higher temperature. At a molding time of 5 min, the blend remains largely uncrosslinked and the glass transition temperature of ENR does not shift much, suggesting that the ENR phase is physically adsorbed onto the filler particles.[28] With an increase in molding time, the glass transition temperature, due to ENR, shifts to the higher value and the blend heterogeneity disappears as well. An increase in molding time has an

Table IV Effect of Filler Loading on Physical Properties and Solvent Swelling of PAA/ENR Blend[a]

Properties	Filler Loading (phr)					
	0	5	10	15	20	25
25% Modulus (MPa)	0.45	0.80	2.35	3.51	7.00	8.00
50% Modulus (MPa)	0.55	0.98	4.11	4.95	—	—
Tensile strength (MPa)	1.61	1.85	5.62	6.90	10.52	11.95
Elongation at break (%)	380	315	123	98	52	45
Hysteresis loss (J/m^2) $\times$ 10^{-3}	3.9	4.6	8.0	13.4	28.3	55.5
Tear strength (N/mm)	10.2	16.6	22.0	24.8	29.6	32.3
Swelling studies:						
(i) Molded Samples:						
(i) Weight Loss[b] (%)	21	16	14	10	3	1
(ii) Nonmolded Samples:						
(i) Bound ENR[c] (%)	0	[e]	24	40	62	68
(i) Bound PAA[d] (%)	0	67	70	75	77	78

[a] Blends mixed at 90 rpm at 180°C; molded at 190°C for 120 min.
[b] Samples were etched with chloroform for 168 h at 25 ± 2°C.
[c] Samples were etched with chloroform (solvent for ENR) for 24 h at 25 ± 2°C.
[d] Samples were etched with methanol (solvent for PAA) for 24 h at 25 ± 2°C.
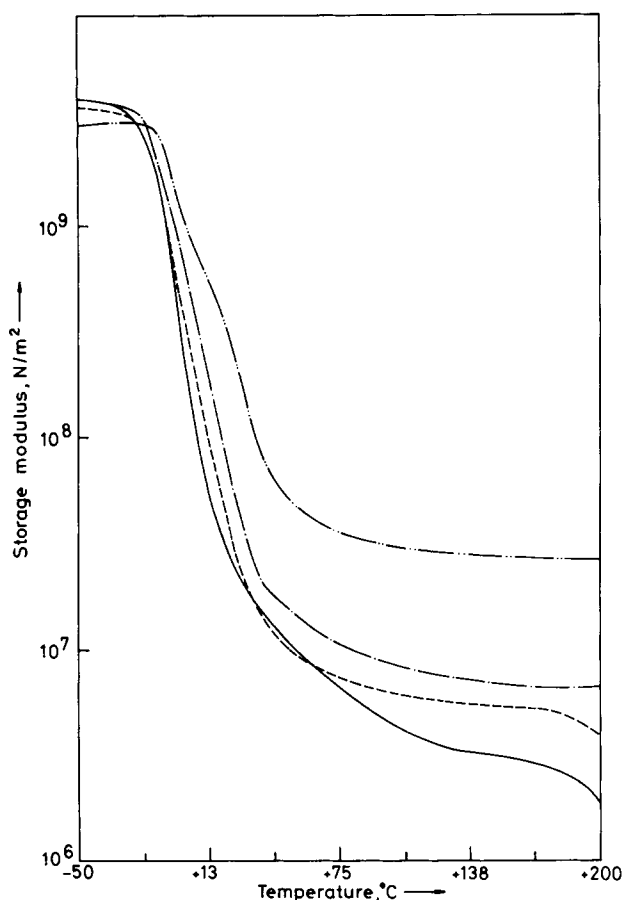[e] Could not be determined.

Figure 7   Effect of molding time on storage modulus vs. temperature plots of 20 phr HAF carbon black-filled 50/50 PAA/ENR blend, (i) (———) 5 min, (ii) (– – –) 30 min, (iii) (– · – · –) 60 min, (iv) (– · · – · · –) 120 min. Blends were mixed by the first technique and were molded at 190°C.

effect similar to the effect for an increase in filler loading. Accordingly, it can be inferred that the carbon black particles are involved in the crosslinking of PAA and ENR. A proposed schematic diagram of the crosslinking of PAA and ENR, through carbon black particles, is presented in Fig. 9. During high temperature molding, the physically adsorbed ENR chains form reactive free radicals. These free radicals are accepted by the black particles, surrounded by PAA, to form an interfacial crosslinked layer. It may be proposed that during crosslinking, the black particles, surrounded by PAA, are surrounded by the interfacial crosslinked layer, due to PAA–ENR network. The formation of this interfacial crosslinked layer, surrounding the carbon black filler particle, is believed to be the cause of the broadening and shifting of the loss peak, due to ENR, to higher tem-

perature. At the low filler loading, however, the amount of physically adsorbed ENR is less and thus the free radical induced crosslinking is also less.

CONCLUSIONS

Carbon black filler (HAF) has a remarkable effect on self-crosslinking of polyacrylic acid and epoxidized natural rubber blend. PAA is believed to be chemisorbed on the carbon black surface, whereas ENR is believed to be adsorbed physically on the filler surface. Crosslinking between PAA and ENR takes place during molding through the carbon black particles and the otherwise inhomogeneous blend becomes homogeneous. The scheme of crosslinking proposed suggests that an interfacial crosslinked layer is formed surrounding the black particles.
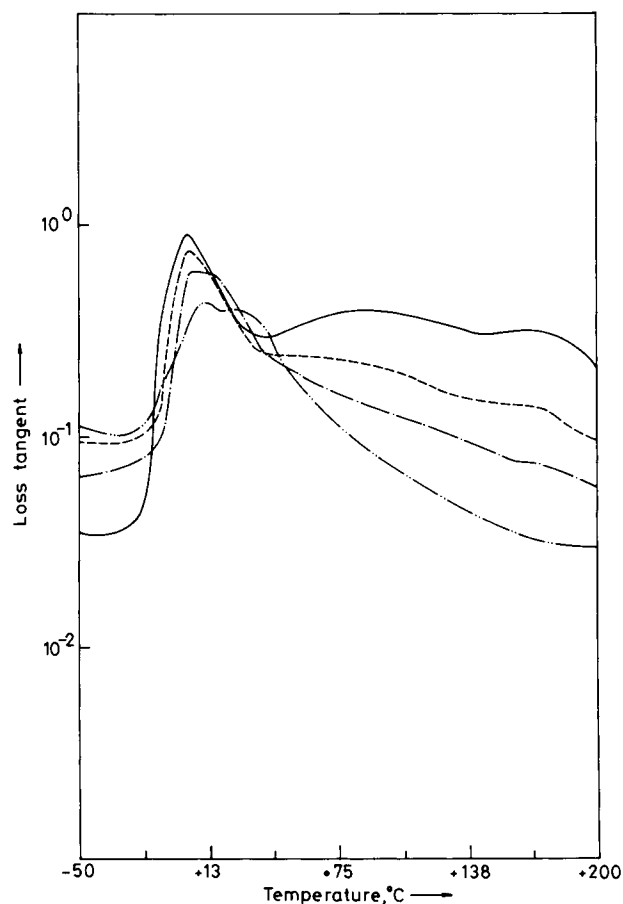

Figure 8   Effect of molding time on loss tangent vs. temperature plots of 20 phr HAF carbon black-filled 50/50 PAA/ENR blend. Description of symbols same as in Figure 7. Blends were mixed by the first technique and were molded at 190°C.
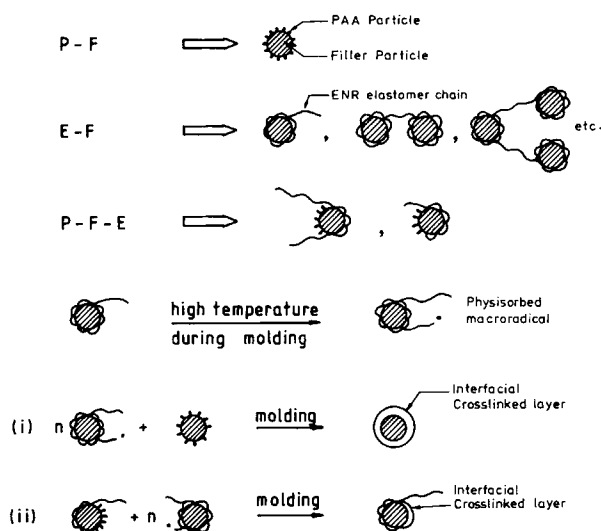
Figure 9   Probable schematic diagram of the crosslinking process in the HAF carbon black-filled blend of PAA and ENR; (P-F) filler particle surrounded by PAA, (E-F) filler particle surrounded by ENR, and (P-E-F) filler particle surrounded by both PAA and ENR.

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