

# Thermally Induced Crosslinking between Polyacrylic Acid and Epoxidized Natural Rubber. III. Effect of Carbon Black Filler and Mixer Rotor Speed

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## SYNOPSIS

High-temperature molding of Brabender-mixed blend of polyacrylic acid (PAA) and epoxidized natural rubber (ENR) causes thermally induced crosslinking between PAA and ENR. Studies on Monsanto rheometry of the blend and physical properties, solvent swelling, and dynamic mechanical properties of the molded blend show that both mixer rotor speed and carbon black filler influence the crosslinking between the component polymers. For example, the extent of crosslinking for the 50–50 PAA–ENR blend was found maximum when the component polymers were mixed at 40 rpm, but the same blend filled with 30 phr HAF carbon black filler showed maximum crosslinking when mixing was carried out at 120 rpm. The results have been explained on the basis of formation of network on the filler surface, which in turn depends on two competing factors: increase in bound rubber formation with increase in filler loading at a fixed rotor speed and enhanced degradation of ENR at higher mixer rotor speed at a fixed filler loading. © 1994 John Wiley & Sons, Inc.

## INTRODUCTION

Recently De and co-workers reported that the blend of polyacrylic acid (PAA) and epoxidized natural rubber (ENR) gets crosslinked during high-temperature molding, and the extent of crosslinking depends on the mixer rotor speed.<sup>1,2</sup> It was also reported that the reinforcing high-abrasion furnace (HAF) carbon black filler influences the thermally induced crosslinking between PAA and ENR.<sup>3</sup> The role of carbon black filler in the vulcanization of rubbers has been studied earlier by several researchers.<sup>4–14</sup>

The present work reports the results of studies on the effects of carbon black filler and mixer rotor speed on the crosslinking between PAA and ENR.

## EXPERIMENTAL

Details of the materials used are given in Table I. The blend composition was 50 : 50 in all mixes.

## Preparation of the PAA–ENR Blends

Mixing was done at 180°C at different rotor speeds of 40, 60, 90, 120, and 150 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 the case of the carbon-black-filled blends, ENR was first masticated for 1 min, then carbon black was added and mixed for another 4 min. Finally PAA was added and the whole mix was blended for additional 10 min. The filler loadings were 10, 20, and 30 parts per 100 parts of total polymer by weight.

## Monsanto Rheometry

Monsanto rheographs of the mixes were taken at 190°C, using Moving Die Rheometer-2000 at an arc of 0.5°.

## Molding

Mixes were molded at 190°C for 120 min under a pressure of 10 MPa in a hydraulic press. The molded samples, while in the mold under pressure, were

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**Table I Details of Materials Used**

Materials	Characteristics	Source
Epoxidized natural rubber, Epoxyprene-50, abbreviated as ENR	$\bar{M}_n = 131^a$ $\bar{M}_w = 446^a$	Kumpulan Guthrie, Berhad, Malaysia
Polyacrylic acid, abbreviated as PAA <sup>b</sup>	Copolymer of acrylic and methacrylic acids, average mol. wt. range 500–1000 <sup>a</sup>	Fluka, Switzerland
Carbon black, HAF (N-330)	BET surface area, 62–68 m <sup>2</sup> /g; average particle dia. 26–35 nm	Phillips Carbon Black Ltd., Durgapur, India

<sup>a</sup> Molecular weight in kg/mol.

<sup>b</sup> In powder form; does not melt even at 400°C.

cooled to room temperature by cold water circulation. Test pieces were cut from the molded sheets.

### Physical Properties

Stress-strain properties were measured at room temperature (25 ± 2°C) using Zwick Universal

Testing Machine Model 1445, according to ASTM D412-87, method A. Hysteresis loss for one cycle was measured under tension mode at a constant strain of 25%. A 90° nick-cut crescent tear test was performed using the same machine according to ASTM D624-86. In all cases the rate of separation of the grips was maintained at 500 mm/min.

**Table II Effect of Mixer Rotor Speed and HAF Carbon Black Filler on Physical Properties of 50–50 PAA–ENR Blends<sup>a</sup>**

Filler Loading (phr)	Rotor Speed (rpm)	25% Modulus (MPa)	Tensile Strength (MPa)	Elongation at Break (%)	Hysteresis Loss × 10 <sup>+3</sup> (J/m <sup>2</sup> )	Tear Strength (N/mm)	ENR Weight Loss <sup>b</sup> (%)
0	40	1.27	4.23	204	3.4	17.6	36
0	60	1.07	3.65	215	3.8	16.6	38
0	90	0.74	2.67	298	4.4	13.1	40
0	120	0.70	2.37	330	4.8	11.3	43
0	150	0.66	2.20	367	5.2	10.0	45
10	40	3.34	6.80	103	10.3	25.1	13
10	60	4.80	7.68	92	16.8	27.2	10
10	90	2.35	5.62	123	8.0	22.0	15
10	120	2.15	4.97	127	7.1	19.2	22
10	150	1.75	4.14	139	5.6	18.3	24
20	40	4.30	6.41	82	14.8	24.3	8
20	60	5.50	7.00	71	19.9	25.0	6
20	90	7.00	10.52	52	28.3	29.6	3
20	120	6.90	9.05	60	25.3	27.6	5
20	150	5.96	8.33	67	24.6	26.4	6
30	40	13.65	15.33	29	63.3	46.8	<sup>c</sup>
30	60	14.84	15.70	29	68.7	46.8	<sup>c</sup>
30	90	15.47	16.60	27	70.4	50.9	<sup>c</sup>
30	120	—	17.40	22	74.3	54.0	<sup>c</sup>
30	150	11.06	12.15	31	55.6	34.3	<sup>c</sup>

<sup>a</sup> Blends molded at 190°C for 120 min.

<sup>b</sup> On solvent swelling.

<sup>c</sup> Negligible.

### Dynamic Mechanical Properties

Dynamic mechanical analyses of the samples ( $3 \times 0.64 \times 0.15 \text{ cm}^3$ ) were carried out using Rheovibron, DDV-III-EP (Orientec Corporation, Japan), under tension mode at a strain amplitude of 0.0025 cm and a frequency of 3.5 Hz. The rate of temperature rise was  $2^\circ\text{C}/\text{min}$ . In another set of experiments, samples were etched with chloroform, a solvent for ENR, and the dynamic mechanical properties of the etched samples were studied under the same conditions.

### Solvent Swelling

Percent weight loss on solvent swelling was calculated by taking the weight of the molded samples after swelling at room temperature ( $25^\circ\text{C}$ ) for 168 h in chloroform, a solvent for ENR. In order to determine bound rubber, the Brabender-mixed blends were allowed to swell in chloroform for 24 h at room

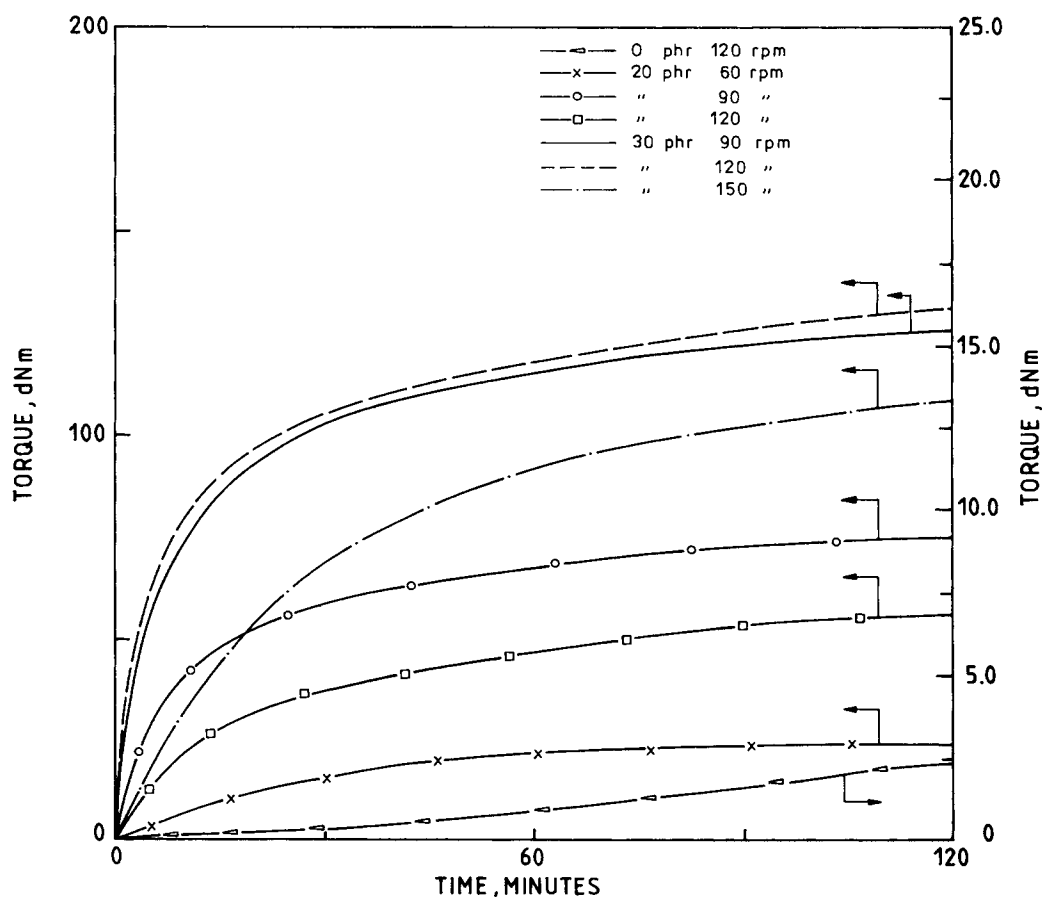
temperature. Swollen samples were dried at  $100^\circ\text{C}$  for 4 h and weighed. Percent bound rubber was calculated with respect to the ENR. The results are summarized in Table II.

### SEM Studies

For morphology studies, the molded samples were fractured under liquid nitrogen. The fractured surfaces were coated with gold and examined under Cam-Scan Series 2 scanning electron microscope (SEM). In another set of experiments, samples were swollen in chloroform (solvent for ENR) for 168 h followed by drying at  $100^\circ\text{C}$  for 4 h. The dried samples were fractured under liquid nitrogen. The fractured surfaces were examined under SEM.

### Electrical Resistivity

Electrical resistance of both nonmolded and molded samples were measured by using a high-resistance



**Figure 1** Effect of mixer rotor speed on Monsanto rheographs of 50-50 PAA-ENR blends. (a) 0 phr filler loading, (— ◁ —) 120 rpm; (b) 20 phr filler loading, (i) (— × —) 60 rpm, (ii) (— ○ —) 90 rpm, (iii) (— □ —) 120 rpm; (c) 30 phr filler loading, (i) (—) 90 rpm, (ii) (---) 120 rpm, (iii) (— · —) 150 rpm.

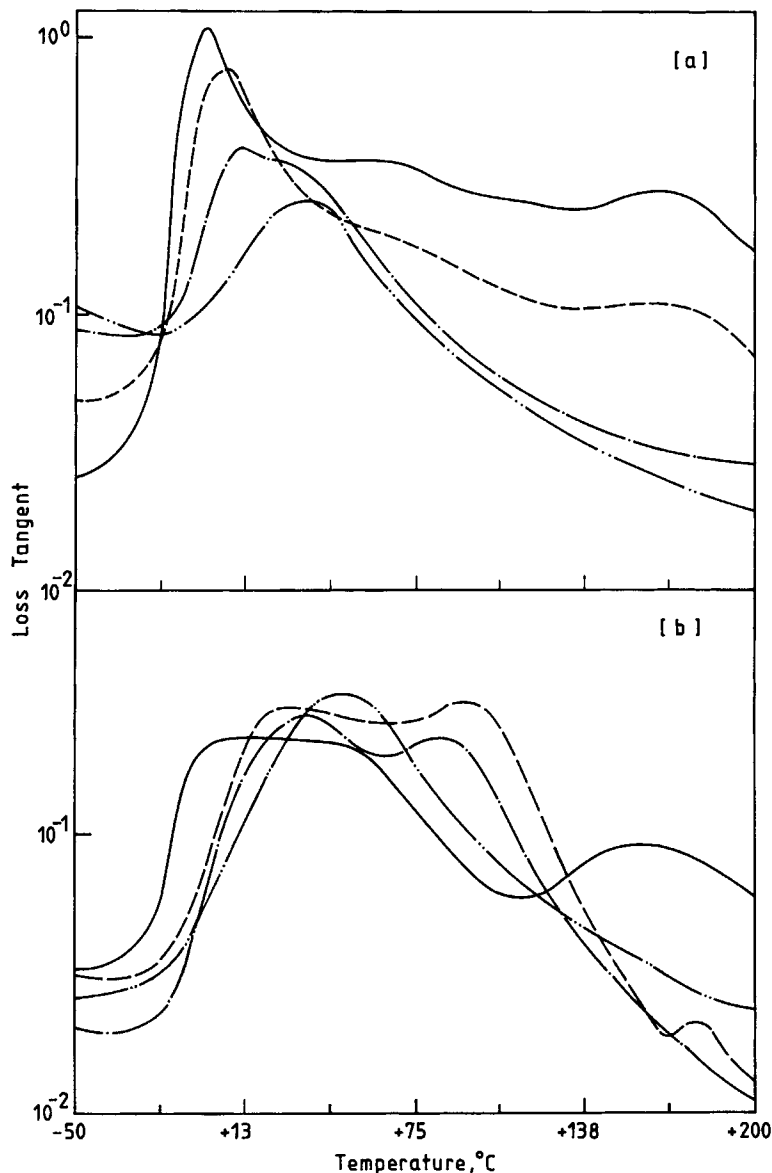
meter (Hewlett-Packard 4329 A) at room temperature. Electrical resistivity ( $\rho$ ) is given by:  $\rho = 19.6/t \times R$ , where  $R$  is the electrical resistance and  $t$  is the thickness of the sample.

## RESULTS AND DISCUSSION

Representative Monsanto rheographs are shown in Figure 1. At any particular filler loading, the rheometric torque increases with increase in curing time

and reaches a plateau around 120 min of curing. At a particular mixer rotor speed, rheometric torque increases with the increase in filler loading. The critical rotor speed ( $N_c$ ) at which the maximum rheometric torque is attained depends on the filler loading. For example, the value of  $N_c$  is 90 rpm for 20 phr filler loading and 120 rpm at a loading of 30 phr.

Figure 2(a) shows the effect of HAF black filler on the variation of loss tangent with temperature. In all cases the mixer rotor speed was 90 rpm. The



**Figure 2** (a) Effect of HAF carbon black filler loading on the variation of loss tangent with temperature of the 50-50 PAA-ENR blends. (i) (—) 0 phr, (ii) (---) 10 phr, (iii) (- · -) 20 phr, (iv) (- · · -) 30 phr. Blends were mixed at 90 rpm and molded at 190°C for 120 min. (b) Loss tangent vs. temperature plots of the chloroform-swollen blends. Symbols same as in Figure 2(a).

unfilled blend registers three peaks: (i) one sharp peak around  $0^{\circ}\text{C}$  due to  $\alpha$  transition of ENR,<sup>15,16</sup> (ii) two broad peaks around  $80$  and  $160^{\circ}\text{C}$  due to  $\beta$  and  $\alpha$  transitions of PAA, respectively.<sup>17,18</sup> Incorporation of carbon black filler into the blend causes (a) gradual disappearance of the broad transitions of PAA and (b) broadening and shifting of the  $\alpha$  transition of ENR to higher temperature. At 30-phr filler loading, one broad transition was observed around  $+50^{\circ}\text{C}$ . Figure 2(b) shows the typical plots of loss tangent versus temperature of the chloroform-etched samples. Chloroform etching is believed to remove free ENR in the molded blend. In absence of the filler, the blend shows two broad transitions, one covering the temperature range of  $0$ – $60^{\circ}\text{C}$ , which is believed to be due to the interfacial crosslinked layer, and the other around  $160^{\circ}\text{C}$  due to the  $\alpha$  transition of PAA. With the increase in filler content, the transition peak due to PAA gradually disappears and at a filler loading of 30 phr one peak around  $+50^{\circ}\text{C}$  appears. This suggests that carbon black filler causes induced homogeneity in the blend composition. In an earlier communication,<sup>3</sup> it has been suggested that during molding bound ENR form active

physisorbed macroradicals, which get crosslinked with sorbed PAA, resulting in the formation of a network, surrounding the filler agglomerate, which is believed to be responsible for inducing homogeneity in HAF-filler-loaded PAA-ENR blends.

Figure 3 shows the effect of molding on the variation of electrical resistivity of PAA-ENR blends at different filler loadings. In conventional carbon-black-filled rubber vulcanizates, crosslinking normally causes decrease in resistivity.<sup>19,20</sup> In the carbon-black-filled PAA-ENR system, however, crosslinking causes increase in resistivity (Fig. 3), presumably due to the formation of PAA-ENR network on the filler surface.

Figures 4(a), 4(b), and 4(c) show the SEM photomicrographs of molded PAA-ENR blends at the filler loadings of 0, 10, and 20 phr, respectively. The unfilled blend was mixed at 40 rpm, whereas 10- and 20-phr filled blends were mixed at 60 and 90 rpm, respectively. It is apparent that with the increase in filler loading, the apparent homogeneity increases. This substantiates the results of dynamic mechanical analyses. Figures 4(d), 4(e), and 4(f) show the SEM photomicrographs of the corre-

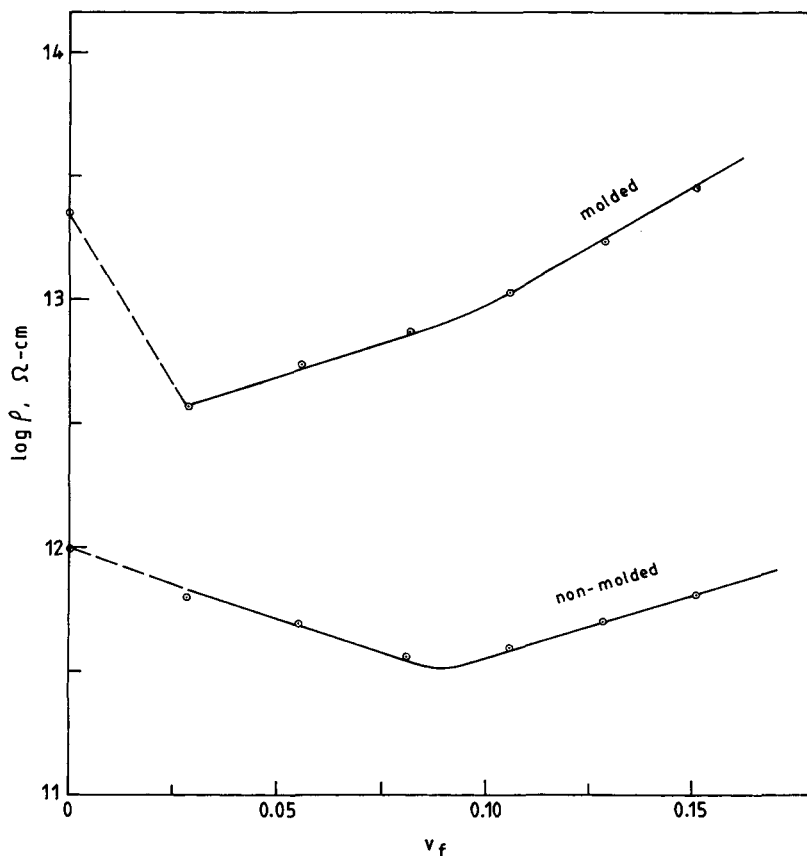
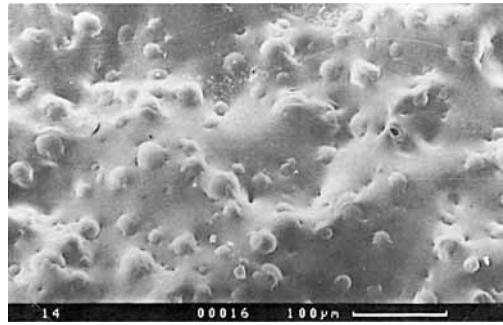
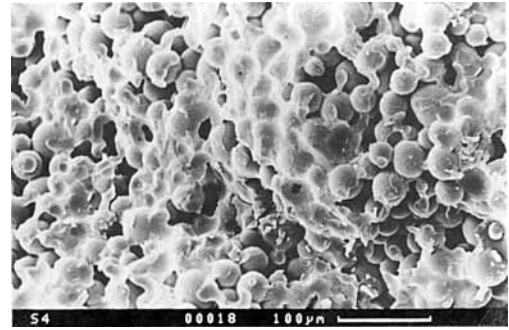


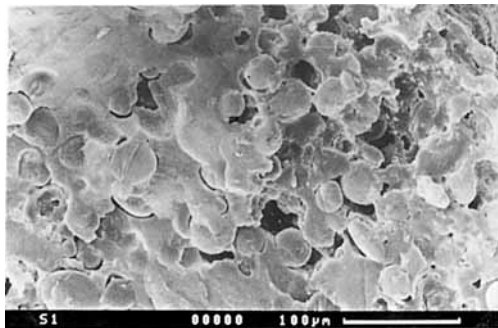
Figure 3 Plot of logarithm of resistivity ( $\log \rho$ ) vs. volume fraction of filler ( $v_f$ ).



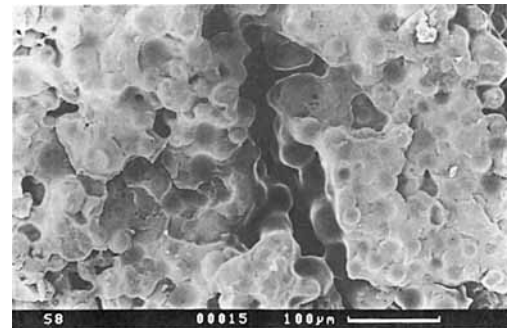
(a)



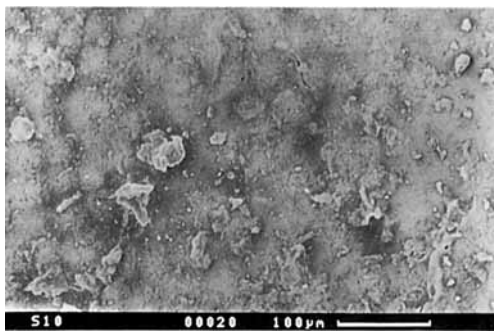
(d)



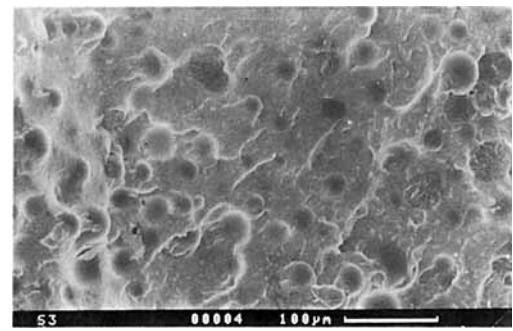
(b)



(e)



(c)



(f)

**Figure 4** SEM photomicrographs of molded blends, (a) unfilled blend, (b) 10-phr filled blend, (c) 20-phr filled blend, (d) chloroform-etched unfilled blend, (e) chloroform-etched 10-phr filled blend, (f) chloroform-etched 20-phr filled blend.

sponding chloroform-etched blends. It is clear that free ENR (which is extractable by chloroform) decreases with the increase in filler loading, indicating increased crosslinking in the presence of the filler. This is further substantiated by the results of weight loss after chloroform extraction (Table II).

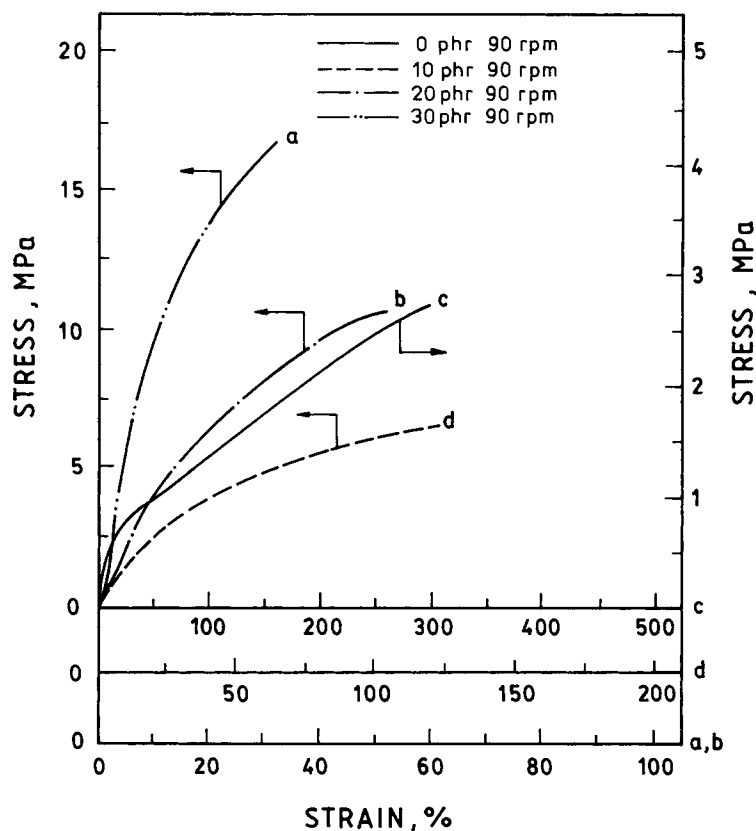
Figure 5 shows the effect of reinforcing carbon black filler on stress-strain plots of the molded blends. Manyfold changes in modulus, tensile strength, and elongation at break values with the increase in filler loading suggests possible participation of carbon black filler not only in the reinforcement of the blend but also in the process of crosslinking between PAA and ENR.

Effect of mixer rotor speed on variation of storage modulus with temperature is shown in Figure 6. It is evident that at 10 and 20 phr filler loadings, storage modulus at room temperature attained a maximum when mixing was carried out at 60 and 90 rpm, respectively. Figure 7 shows similar plots for the unfilled and 30-phr carbon-black-filled blends, and maximum in the modulus was observed when mixing was done at 40 and 120 rpm, respectively.

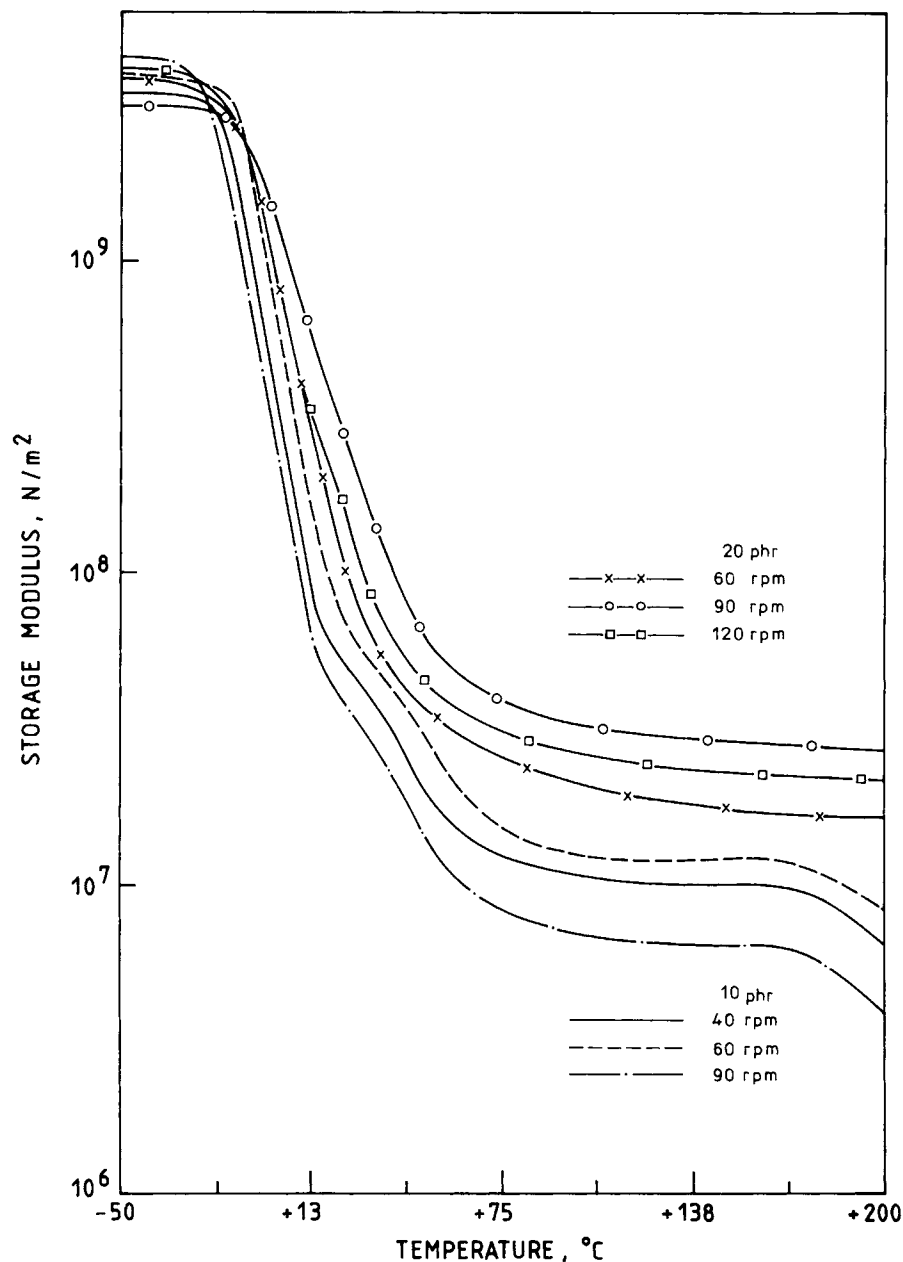
Increase in extent of crosslinking is reported to be responsible for the increase in storage modulus.<sup>21,22</sup> Accordingly, it is believed that at a particular filler loading the extent of crosslinking increases with the increase in mixer rotor speed and attains a maximum at a particular rotor speed, called critical rotor speed ( $N_c$ ), beyond which the extent of crosslinking decreases. The value of  $N_c$  increases with the increase in filler loading.

Figures 8 and 9 show the effect of the carbon black filler on the variation of loss tangent with temperature at different mixer rotor speeds. For the unfilled and 10-, 20-, 30-phr filled blends, maximum in loss peak value was found when mixing was performed at 40, 60, 90, and 120 rpm, respectively. Since increase in crosslink density lowers the loss peak value,<sup>23-25</sup> it can be inferred that at a filler loading, extent of crosslinking registers maximum when mixing was done at  $N_c$ .

Figure 10 shows the plots of  $(\tan \delta_{\max})_f / (\tan \delta_{\max})_0$  versus mixer rotor speed, where  $(\tan \delta_{\max})_f / (\tan \delta_{\max})_0$  is the ratio of loss peak values of the filled and unfilled blends. It is apparent that (a)



**Figure 5** Effect of filler loading on stress-strain plots of the 50-50 PAA-ENR blends. (i) (—) 0 phr, (ii) (---) 10 phr, (iii) (-·-) 20 phr, (iv) (-··-) 30 phr. Blends were mixed at 90 rpm and molded at 190°C for 120 min.



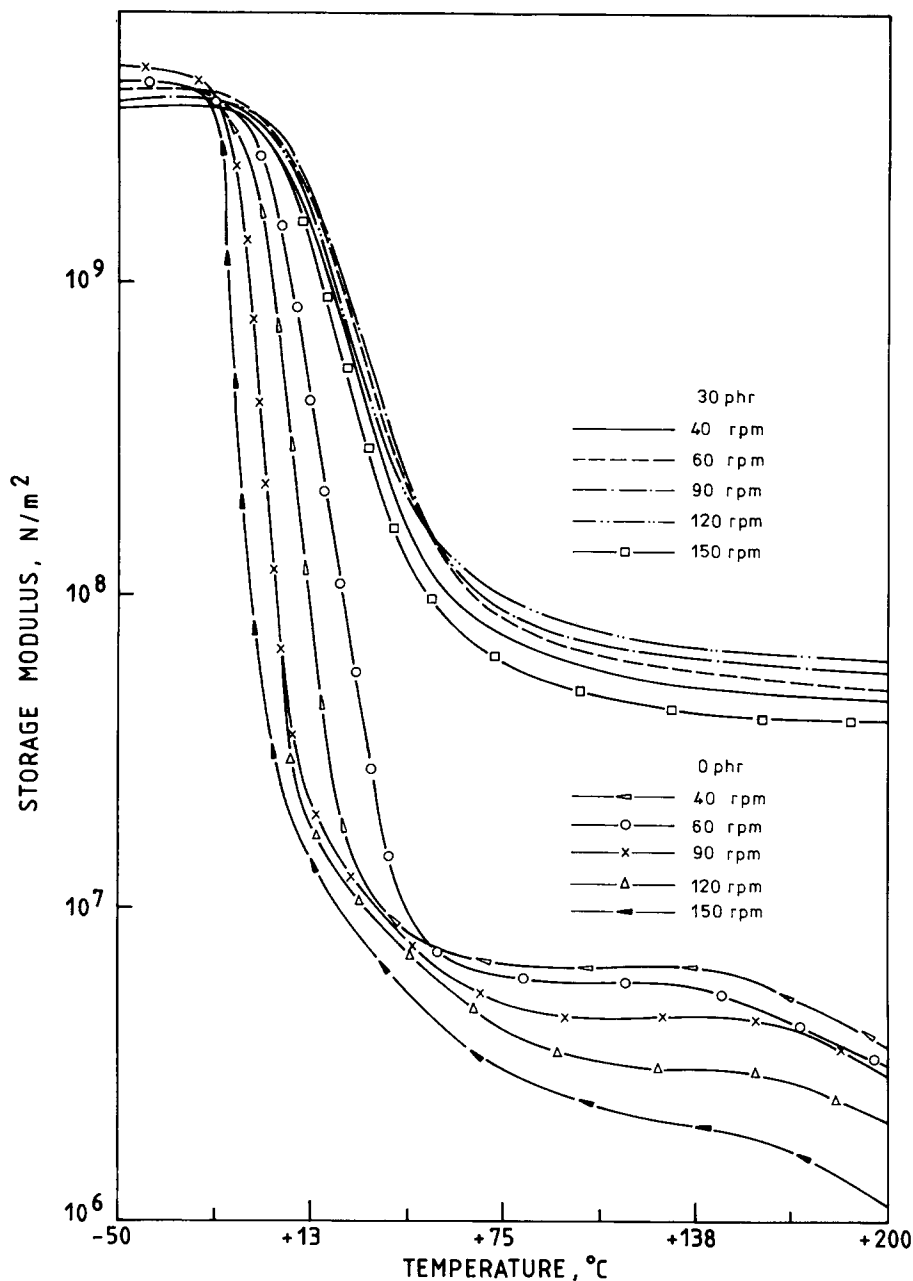
**Figure 6** Effect of mixer rotor speed on the variation of storage modulus with temperature of the 50-50 PAA-ENR blends. (a) 10-phr filler loading, (i) (—) 40 rpm, (ii) (---) 60 rpm, (iii) (-·-) 90 rpm. (b) 20-phr filler loading, (i) (-×-) 60 rpm, (ii) (-○-) 90 rpm, (iii) (-□-) 120 rpm. Blends were molded at 190°C for 120 min.

at a particular rotor speed the ratio of loss peak values decreases sharply with the increase in filler loading and (b) at a particular filler loading the ratio decreases and attains a minimum at  $N_c$ .

The effect of carbon black filler loading and mixer rotor speed on the physical properties and swelling characteristics are shown in Table II. It is apparent

that physical properties increase with the increase in mixer rotor speed up to  $N_c$ , beyond which the properties fall down. Figure 11 shows the plot of bound rubber at various mixer rotor speeds and filler loadings. It is evident that the bound rubber reaches a maximum at  $N_c$  for each filler loading. Thus there exists a correlation between bound rubber formation

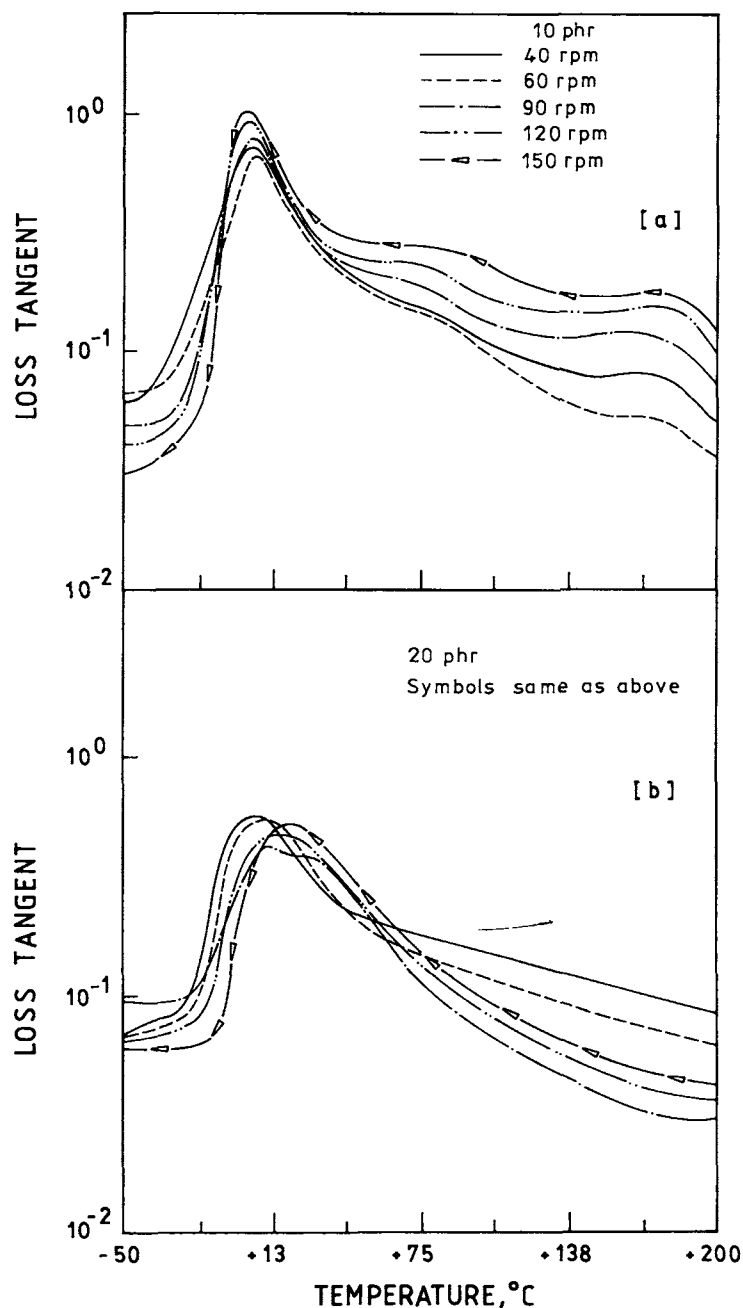




**Figure 7** Effect of mixer rotor speed on the variation of storage modulus with temperature of the 50-50 PAA-ENR blends. (a) 0-phr filler loading, (i) ( $\leftarrow \triangleleft$ ) 40 rpm, (ii) ( $\leftarrow \circ \leftarrow$ ) 60 rpm, (iii) ( $\leftarrow \times \leftarrow$ ) 90 rpm, (iv) ( $\leftarrow \triangle \leftarrow$ ) 120 rpm, (v) ( $\leftarrow \blacktriangleleft \leftarrow$ ) 150 rpm. (b) 30-phr filler loading, (i) ( $\leftarrow$ ) 40 rpm, (ii) ( $\leftarrow \cdot \leftarrow$ ) 60 rpm, (iii) ( $\leftarrow \cdot \cdot \leftarrow$ ) 90 rpm, (iv) ( $\leftarrow \cdot \cdot \cdot \leftarrow$ ) 120 rpm, (v) ( $\leftarrow \square \leftarrow$ ) 150 rpm. Blends were molded at 190°C for 120 min.

and physical properties. It is apparent that the higher the bound rubber, the higher the extent of crosslinking. Table II further reveals that weight loss on solvent swelling became minimum at  $N_c$ , indicating maximum extent of crosslinking. From

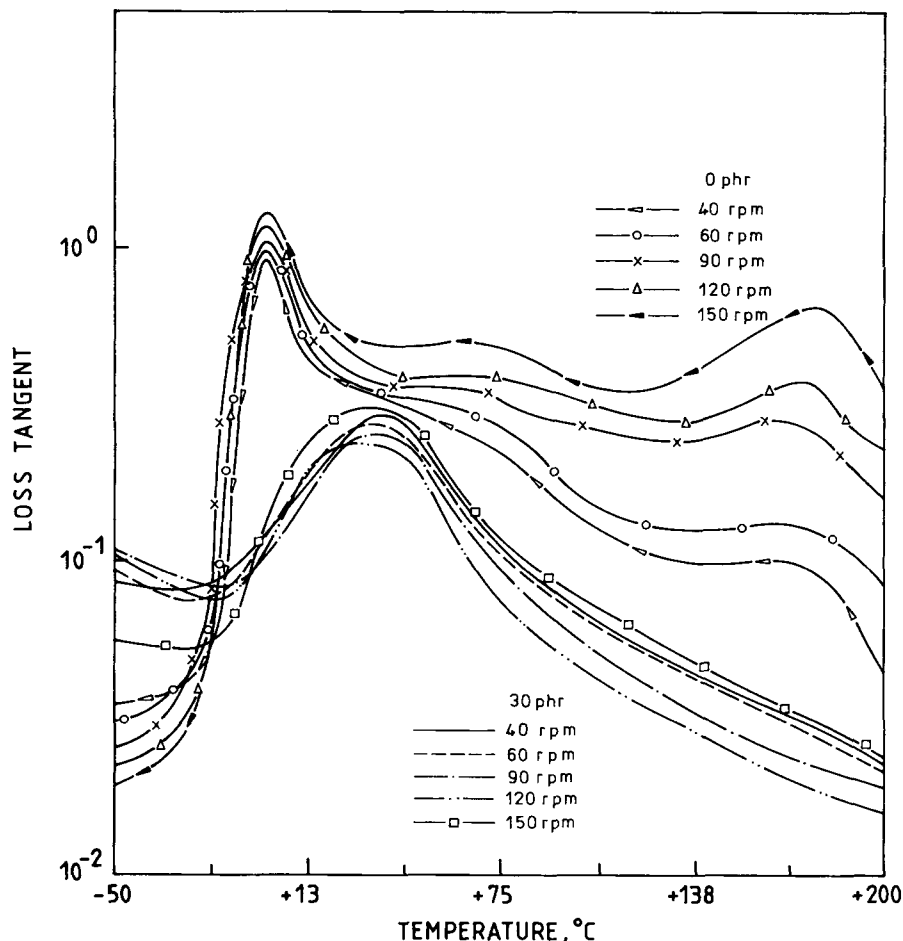
Table II it is evident that for the unfilled blend, mixing at high rotor speed causes a fall in the physical properties. This is believed to be due to the decrease in the extent of crosslinking at higher mixer rotor speeds. It has been reported that epoxy groups



**Figure 8** Effect of mixer rotor speed on the variation of loss tangent with temperature of the 50-50 PAA-ENR blends. (a) 10-phr filler loading, (i) (—) 40 rpm, (ii) (---) 60 rpm, (iii) (-·-) 90 rpm, (iv) (-·-·) 120 rpm, (v) (-◁-) 150 rpm. (b) 20-phr filler loading. Symbols same as in Figure 8(a). Blends were molded at 190°C for 120 min.

of ENR react with the carboxylic acid groups during molding.<sup>1</sup> Epoxy groups are strained and during mixing at higher rotor speed, opening of these groups may lead to the breakdown of ENR chains.<sup>2</sup> Thus during molding availability of epoxy groups for crosslinking becomes less if the components are

mixed at higher rotor speed. Presence of carbon black helps sorption of elastomer free radicals on its surface during mixing.<sup>26-34</sup> As a result of this, the breakdown process of ENR is inhibited. As the mixer rotor speed increases, dispersion of filler also increases along with the generation of active filler sur-



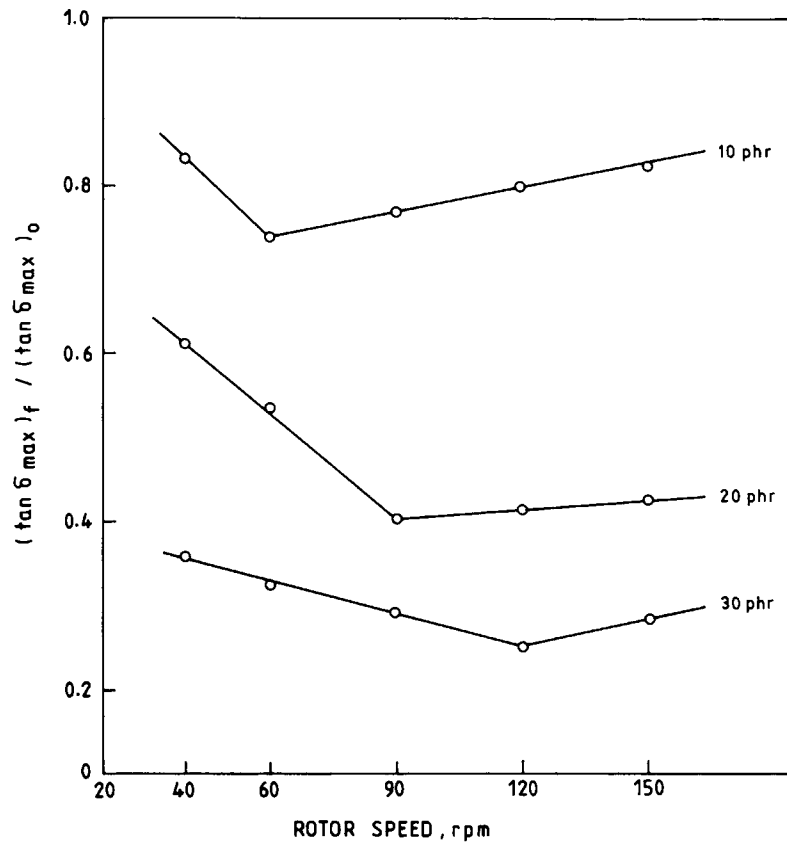
**Figure 9** Effect of mixer rotor speed on the variation of loss tangent with temperature of the 50-50 PAA-ENR blends; symbols same as in Figure 4. Blends were molded at 190°C for 120 min.

face, which results in an increase in bound rubber content.

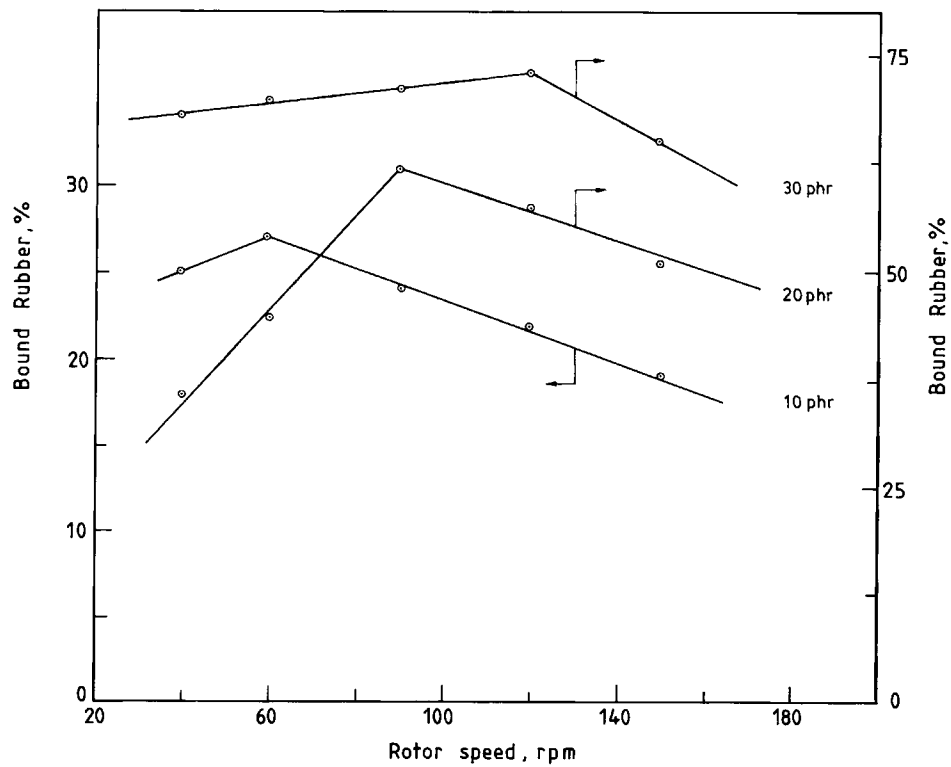
There exists two competing factors during mixing of the component polymers in the presence of carbon black filler. First, with the increase in mixer rotor speed, dispersion of filler along with the sorption of ENR chains increases, as a result of which crosslinking increases. Second, increased mixer rotor speed helps degradation of ENR chains, inhibiting the crosslinking process. At any particular filler loading the sorption process dominates over the breakdown process when mixing is carried out at low rotor speed (i.e., below  $N_c$ ). At higher rotor speed the breakdown process increases and ultimately is believed to dominate over the sorption process beyond  $N_c$  at that filler loading. It is expected that with the increase in filler loading, sorption of ENR increases, and obviously higher rotor speed is

required for the breakdown process to dominate over the sorption process. This is why the value of critical rotor speed increases with the increase in filler loading.

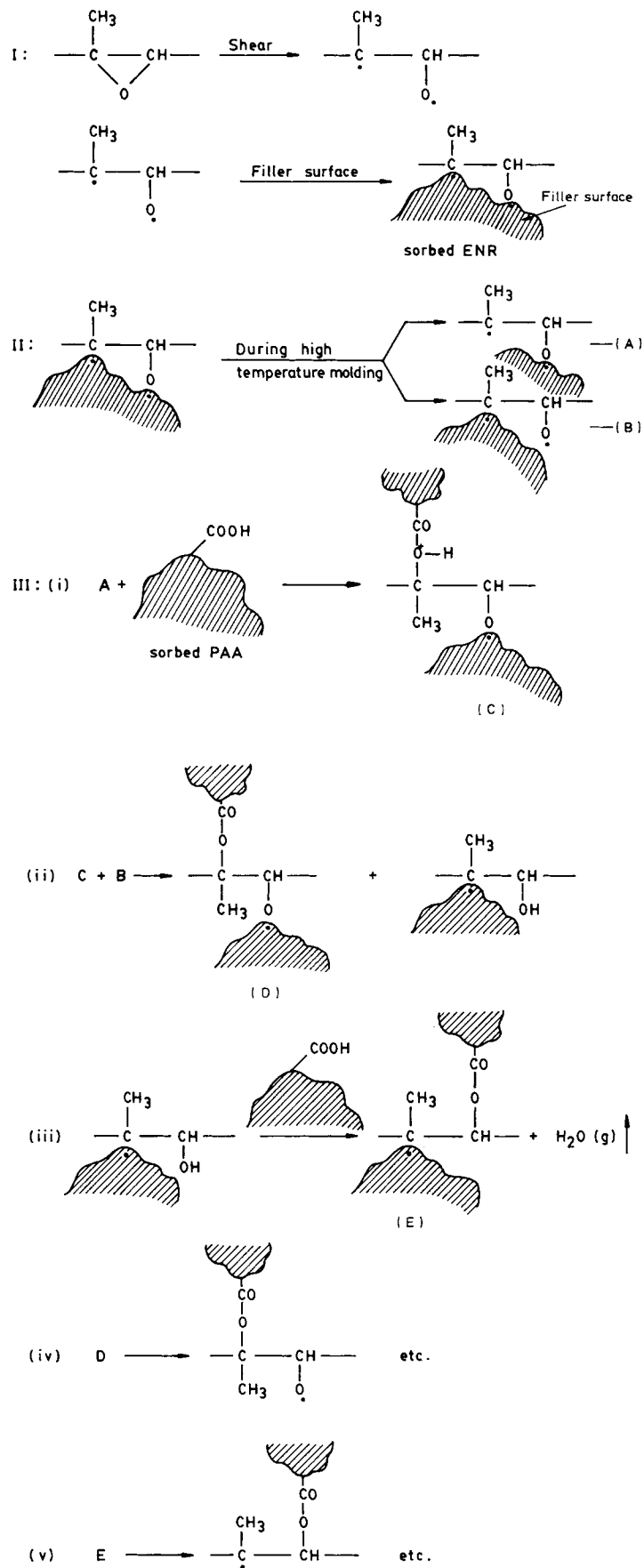
PAA is highly polar and is likely to be chemisorbed onto the filler surface, and it has been reported that sorbed PAA, during molding, gets reacted with physisorbed macroradical, generated from bound ENR.<sup>3</sup> Figure 12 shows plausible mechanism of crosslinking in presence of filler: (a) During molding two types of physisorbed macroradicals (*A* and *B*) may be generated. It may be observed that when the free radical *A* interacts with sorbed PAA, the crosslinking process continues to form several crosslinked species, like *D* and *E*. (b) The crosslinked species may further initiate crosslinking through the generation of active free radicals. This illustrates how carbon black enhances the cross-



**Figure 10** Plots of ratio of loss peak values vs. mixer rotor speed;  $(\tan \delta_{\max})_f$ , loss peak value for the filled system at a particular rotor speed and  $(\tan \delta_{\max})_o$ , loss peak value for the unfilled system mixed at the same rotor speed.



**Figure 11** Plot of bound rubber vs. mixer rotor speed at different filler loadings.



**Figure 12** Plausible mechanism of crosslinking between ENR and PAA in presence of HAF carbon black filler during molding.

linking between PAA and ENR. With the increase in filler loading, bound ENR increases, and hence the concentration of active free radicals ( $A$  and  $B$ ) increases, resulting in an increase in crosslinking.

## CONCLUSIONS

Presence of HAF carbon black largely influences the crosslinking process between PAA and ENR. The extent of crosslinking increases with the increase in mixer rotor speed, until a critical rotor speed,  $N_c$ , is reached. Mixing at a rotor speed higher than  $N_c$  causes decrease in the extent of crosslinking. The value of  $N_c$  depends on the filler loading, for example,  $N_c$  is 60 rpm for 10 phr, 90 rpm for 20 phr, and 120 rpm for 30 phr. It is believed that in presence of filler, mechanochemical degradation of ENR chains is markedly reduced owing to the sorption of ENR chains onto the filler surface, but the former (degradation) dominates over the latter (sorption) when mixing is carried out beyond  $N_c$ .

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