

# Effect of HAF Carbon Black Filler on Chemorheological Behavior of Poly(acrylic acid)–Epoxidized Natural Rubber Blend

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Received 9 May 1995; accepted 7 October 1995

**ABSTRACT:** Brabender-mixed blends of poly(acrylic acid) (PAA) and epoxidized natural rubber (ENR) were extruded through the capillary in a Monsanto processability tester, and the capillary pressure versus extrusion time plots were recorded. Constancy in capillary pressure with extrusion time was observed in the case of PAA/ENR blend; but the same blend, filled with HAF carbon black filler, shows a steady increase in capillary pressure with extrusion time. In presence of a free radical acceptor like thiophenol, the rate of capillary pressure rise decreases. Measurements of physical properties, swelling studies, and scanning electron microscopy photomicrography of the extrudates indicates the occurrence of a chemical interaction between physisorbed ENR and chemisorbed PAA. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **65**: 135–142, 1997

**Key words:** poly(acrylic acid); epoxidized natural rubber; HAF carbon black; sorption; chemical interaction; free radical acceptor; chemorheology; physical properties; activation energy

## INTRODUCTION

It has been reported earlier that a Brabender-mixed blend of poly(acrylic acid) (PAA) and epoxidized natural rubber (ENR) undergoes crosslinking when molded at high temperature and pressure.<sup>1</sup> The rate and extent of crosslinking increases in the presence of HAF carbon black filler.<sup>2,3</sup> It is believed that interfacial crosslinking between PAA and ENR takes place in the presence of carbon black to form a filler agglomerate superstructure.<sup>4</sup> The present article reports the results of processability studies of PAA/ENR blends in a Monsanto processability tester (MPT) with special reference to the effect of carbon black filler. Several investigators have studied the rheological behavior of elastomers,<sup>5,6</sup> as well as some plastic–rubber blends.<sup>7–10</sup> Rheological behavior of

carbon black filled elastomers is well documented in the literature.<sup>11–14</sup> The role of fillers in the flow behavior of plastic–rubber blends has also been studied.<sup>15–18</sup> Han et al.<sup>19–21</sup> reported the chemorheology of thermosetting polyester resins.

## EXPERIMENTAL

The details of the materials used are given in Table I. The PAA/ENR blend composition was 50 : 50 (by weight) in all mixes. The filler loadings used were 5, 10, and 20 parts per 100 parts of the total polymer by weight.

### Preparation of the PAA/ENR Blends

Mixing was done in a Brabender Plasticorder PLE 330 at 180°C at the rotor speed of 90 rpm. Fill factor was maintained at 0.85 in all cases. In the case of the unfilled blend, ENR was masticated

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**Table I** Details of the Materials Used

Materials	Characteristics	Source
Epoxidized natural rubber, Epoxyprene-50, abbreviated as ENR	$\bar{M}_n = 131^a$ $\bar{M}_w = 446^a$	Kumpulan Gutherie (Berhad, Malaysia)
Poly (acrylic acid), abbreviated as PAA	Average molecular weight range $\bar{M}_w = 500-1000$ ; <sup>a</sup> does not melt, even at 400°C	Fluka (Switzerland)
Carbon black HAF (N330)	BET surface area, 62–88 m <sup>2</sup> /g; particle diameter, 23 nm	Philips Carbon Black Ltd. (Durgapur, India)
Thiophenol	Molecular weight = 0.11; <sup>a</sup> Specific gravity = 1.078	Johnson Matthey (Germany)

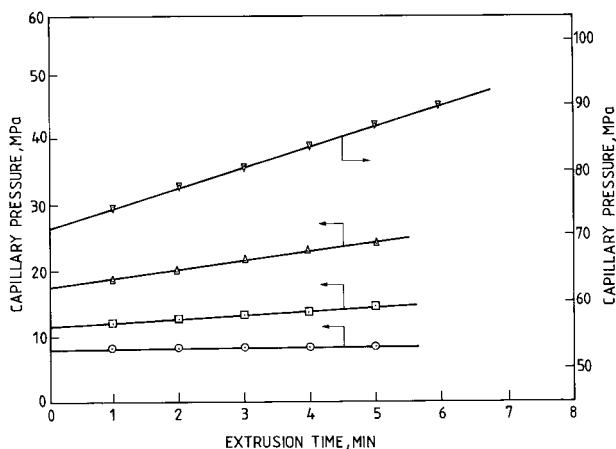
<sup>a</sup> Molecular weight in kg/mol.

for 1 min, followed by blending with PAA for another 10 min. The mix was quickly passed through a laboratory-size two-roll mill to sheet out the material. In the case of the carbon black filled blends, ENR was masticated for 1 min, then carbon black was added and mixed for another 4 min. Finally, PAA was added, and the mix was blended for another 10 min.

For mixes containing thiophenol, ENR was masticated for 1 min, then thiophenol was added and mixed for 30 s. Next, carbon black was added and mixed for 4 min. Finally, PAA was added and blended for another 10 min.

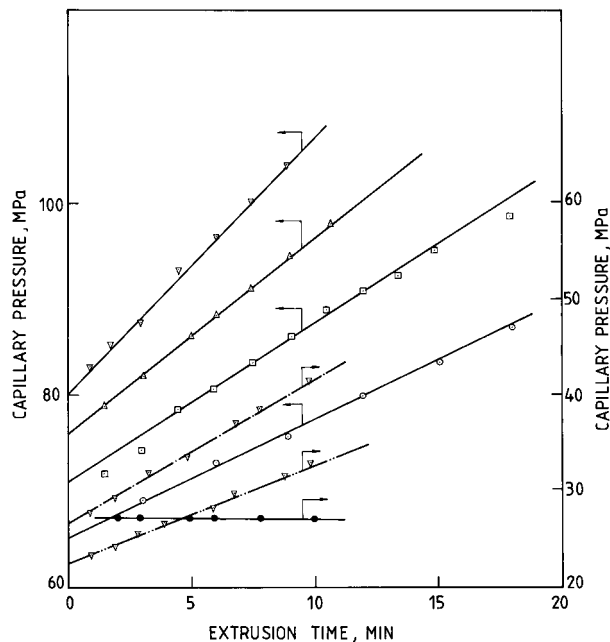
### Rheological Properties

Flow properties of the compounds were measured by a MPT, which is a fully automatic high-pres-



**Figure 1** Plots of capillary pressure versus extrusion time for PAA-ENR blends containing different HAF carbon black filler loadings: 0 phr (—○—); 5 phr (—□—); 10 phr (—△—); 20 phr (—▽—). Extrusion temperature, 170°C; shear rate, 98.4 s<sup>-1</sup>.

sure capillary viscometer. The entire barrel and capillary are electrically heated with a microprocessor-based temperature controller. The details of the instruments are available in the literature.<sup>22,23</sup> The capillary used had a length-to-diameter ratio of 30 : 1, having multiple cone entry



**Figure 2** Plots of capillary pressure versus extrusion time. (a) PAA-ENR blends containing 20 phr carbon black, extruded under different shear rates: 24.6 s<sup>-1</sup> (—○—); 61.5 s<sup>-1</sup> (—□—); 98.4 s<sup>-1</sup> (—△—); 123 s<sup>-1</sup> (—▽—). Extrusion temperature, 150°C. (b) ENR containing 20 phr carbon black extruded under the shear rate of 123 s<sup>-1</sup> (—●—). (c) 20 phr filler loaded blend containing 2 phr thiophenol (—▽— · —▽—); 20 phr filler loaded blend containing 5 phr thiophenol (—▽— · · —▽—). Extrusion shear rate was 123 s<sup>-1</sup>.

**Table II Effect of Filler Loading on the Physical Properties of Extrudates**

Filler Loading (phr)	50% Modulus (MPa)	Tensile Strength (MPa)	Elongation at Break (%)	Unextractable ENR (%)
0	0.60	0.65	780	—
5	0.70	0.99	434	28
10	0.91	1.38	282	45
20	2.21	2.37	74	74

Extrusion shear rate:  $98.4 \text{ s}^{-1}$ ; extrusion temperature:  $150^\circ\text{C}$ .

with compound entrance angles of 45 and 60 degrees. The barrel and the capillary diameters were 19.06 and 1 mm, respectively. The preheat time used for each sample was 3 min. The rate of shear variation was achieved by automatically changing the speed of the plunger. During the extrusion, a plot of capillary pressure against extrusion time was recorded automatically.

To calculate activation energy, the following two sets of experiments were carried out: (1) blends with varying filler contents were extruded under the constant shear rate of  $98.4 \text{ s}^{-1}$  and at three different temperatures of 130, 150, and  $170^\circ\text{C}$ ; and (2) blends containing 20 phr carbon black and thiophenol, a known free radical acceptor, were extruded under a shear rate of  $123.0 \text{ s}^{-1}$  at two different temperatures of 150 and  $170^\circ\text{C}$ .

### Solvent Swelling

Chloroform, a solvent for ENR, was used for swelling studies. For determination of unextractable ENR, extrudates were allowed to swell in chloroform for 24 h at room temperature. In all cases, swollen samples were dried at  $100^\circ\text{C}$  for 4 h and weighed. Calculations were based on ENR content of the blend.

### Physical Properties

Physical properties of the extrudates were measured by a Zwick universal testing machine,

Model 1445, at room temperature. Rate of separation of the grips was 500 mm/min. The area of cross section of the extrudates were calculated from their diameters. Four sets of extrudate samples were collected for testing (1) Blends containing different filler loadings were extruded at  $150^\circ\text{C}$  under the shear rate of  $98.4 \text{ s}^{-1}$  (2) In the case of the blend containing 20 phr HAF carbon black filler, extrudates were collected after 10 min of extrusion at  $150^\circ\text{C}$  under varying shear rates of 24.6, 61.5, 98.4, and  $123.0 \text{ s}^{-1}$ . (3) In the case of the blend containing 20 phr HAF carbon black filler, extrusion was done at  $150^\circ\text{C}$  under a shear rate of  $123.0 \text{ s}^{-1}$ , and extrudates were collected after different extrusion times, for example, 2.5, 5.0, 7.5, and 10 min. (4) Blends containing 20 phr HAF carbon black and thiophenol, were extruded at  $150^\circ\text{C}$  under a shear rate of  $123.0 \text{ s}^{-1}$ , and the extrudates were collected for testing. In all cases, samples after extrusion were first allowed to cool to room temperature, kept for 24 h, and then tested.

### Scanning Electron Microscopy Studies

Electron microscopic studies of different samples were conducted in a Cam-Scan Series-2 scanning electron microscope.

## RESULTS AND DISCUSSION

Figure 1 shows the capillary pressure versus extrusion time plots for PAA/ENR blends. It was

**Table III Effect of Shear Rate on Physical Properties of Extrudates**

Shear Rate ( $\dot{\gamma}$ ) ( $\text{s}^{-1}$ )	50% Modulus (MPa)	Tensile Strength (MPa)	Elongation at Break (%)	Unextractable ENR (%)
24.6	1.98	2.06	100	66
61.5	2.13	2.23	84	71
98.4	2.21	2.37	74	74
123.0	2.34	2.59	67	78

Filler loading: 20 phr; extrusion temperature:  $150^\circ\text{C}$ ; extrusion time: 10 min.

**Table IV** Effect of Extrusion Time on the Physical Properties of the Extrudates

Run Time (min)	50% Modulus (MPa)	Tensile Strength (MPa)	Elongation at Break (%)	Unextractable ENR (%)
2.5	1.48	1.75	118	67
5.0	1.61	1.81	104	71
7.5	1.92	2.17	79	74
10.0	2.34	2.59	67	78

Filler loading: 20 phr; extrusion temperature: 150°C; extrusion shear rate: 123 s<sup>-1</sup>.

observed that capillary pressure did not change with extrusion time for the PAA/ENR blend. Presence of carbon black filler in the blend, however, causes an increase in capillary pressure with extrusion time, and the rate of pressure rise increases with the increase in filler loading. Figure 2 shows the effect of shear rate on the rate of capillary pressure rise in the case of the blend containing 20 phr HAF carbon black. It is evident that the rate of capillary pressure rise increases with the increase in shear rate.

Tables II–IV summarize the effects of filler loading, shear rate, and extrusion time on the physical properties of the extrudates. It is evident that an increase in filler loading, shear rate, and extrusion time causes an increase in modulus and tensile strength but a decrease in elongation at break. Solvent swelling results show that the proportion of nonextractable ENR increases with the increase in filler loading, shear rate, and extrusion time. When a mixture of ENR and carbon black is extruded through the capillary, there was no pressure rise (Fig. 2) as was observed in the case of PAA/ENR blend. Therefore, the pressure rise in the capillary during extrusion in the case of PAA/ENR/carbon black system must be due to an interaction between PAA and ENR activated by the carbon black, and the extent of interaction increases with the increase in filler loading, shear rate, and extrusion time.

It has been observed from Figures 1 and 2 that capillary pressure rises linearly with time, such that

$$\frac{d(\Delta P)}{dt} = m \quad (1)$$

where  $\Delta P$  is the capillary pressure increment at any time  $t$ , and  $m$  is the constant for a particular blend and can be found out from Figures 1 and 2.

Assuming the capillary pressure rise to be due to filler-induced PAA/ENR interaction, following Lodge,<sup>24</sup> it can be argued that

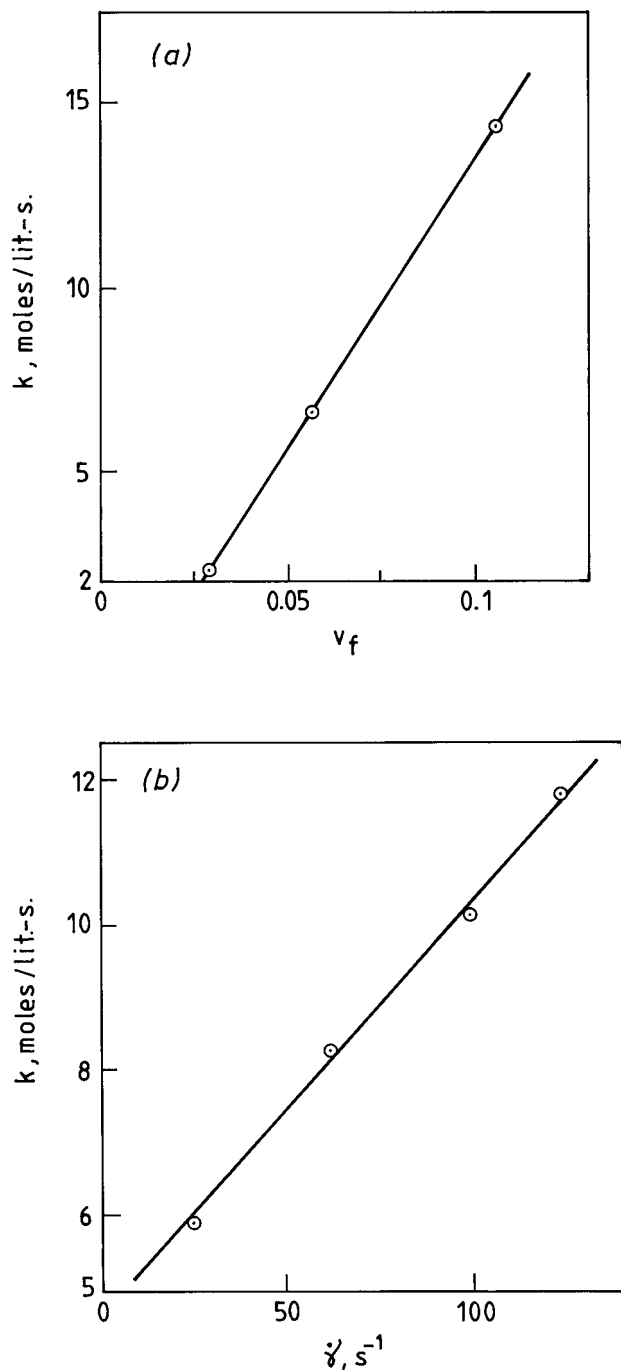
$$\Delta P = C_{\alpha} RT \quad (2)$$

where  $C_{\alpha}$  is the extent of interaction,  $R$  is the molar gas constant, and  $T$  is the extrusion temperature.

From eqs. (1) and (2), we can write that at a particular temperature and shear rate

$$\frac{dC_{\alpha}}{dt} = \frac{m}{RT} = k \quad (3)$$

where  $\frac{dC_{\alpha}}{dt}$  is the rate of interaction, and  $k$  is the rate constant. Equation (3) suggests that the interaction during extrusion follows zero-order kinetics. At any particular filler loading, the concentrations of functional groups in the polymers and active sites on the carbon black surface are sufficiently high, making the rate of chemical interaction independent of the concentrations of the constituent polymers. In gum, PAA/ENR blend activation energy of the chemical interaction between PAA and ENR is believed to be high enough to preclude the occurrence of the proposed chemical interaction during extrusion. Presence of filler is presumed to reduce the activation energy of chemical interaction between PAA and ENR. Thus, the activation energy of chemical interaction decreases with an increase in filler loading, and, hence, the rate constant of chemical interaction increases. Figure 3(a) shows the variation of rate constant with volume fraction of filler at constant shear rate and extrusion temperature. Figure 3(b) shows the variation of rate constant with shear rate at constant filler loading and extrusion



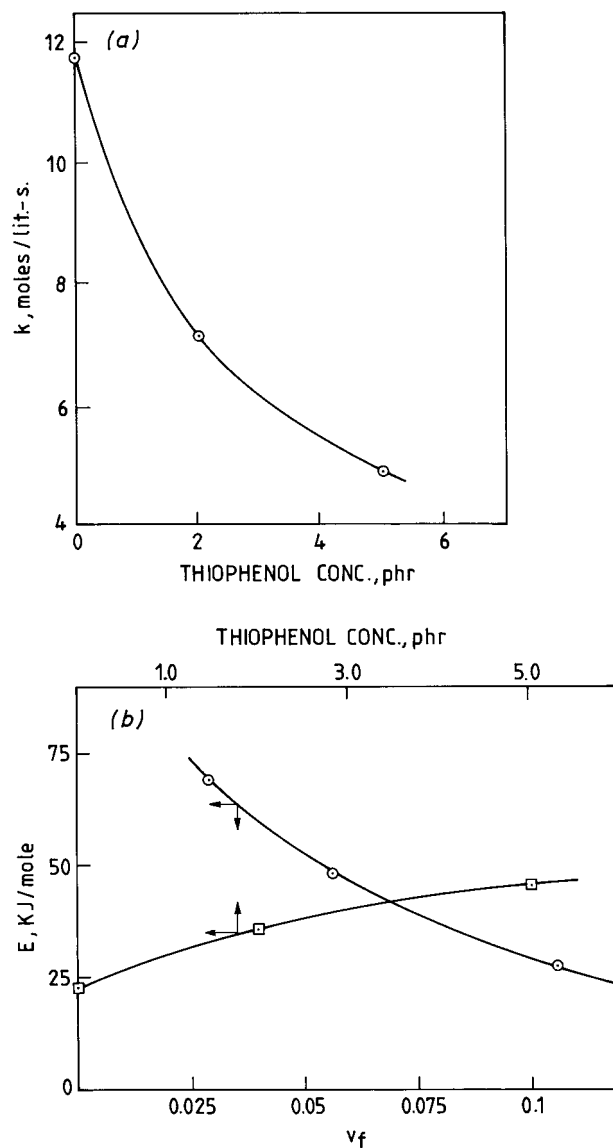
**Figure 3** (a) Plots of reaction rate constant ( $k$ ) versus volume fraction of filler ( $v_f$ ) in the case of PAA-ENR-carbon black system, extruded at 170°C under a shear rate of 98.4  $s^{-1}$ . (b) Plots of reaction rate constant ( $k$ ) versus shear rate ( $\dot{\gamma}$ ) in the case of PAA-ENR-20 phr HAF carbon black system, extruded at 150°C.

temperature. Activation energy of the interaction has been calculated by using the Arrhenius equation, as follows:

$$\ln(k_1/k_2) = -(E/R)[1/T_1 - 1/T_2],$$

$$T_2 > T_1 \quad (4)$$

where  $k_1$  and  $k_2$  are the rate constants at the temperatures  $T_1$  and  $T_2$ , respectively;  $E$  is the activation energy, and  $R$  is the molar gas constant. Figure 4(b) shows the variation of activation energy of interaction with filler loading. The progressive reduction in the activation energy of interaction



**Figure 4** (a) Plots of the reaction rate constant ( $k$ ) versus thiophenol concentration in the case of PAA-ENR-20 phr HAF carbon black system containing thiophenol extruded at 150°C under a shear rate of 123  $s^{-1}$ . (b) plots of activation energy ( $E$ ) versus filler loading (—○—); activation energy ( $E$ ) versus thiophenol concentration (—□—).

**Table V** Effect of Thiophenol Concentration on the Physical Properties of the Extrudates

Thiophenol Concentration (phr)	50% Modulus (MPa)	Tensile Strength (MPa)	Elongation at Break (%)	Unextractable ENR (%)
0	2.34	2.59	67	78
2	0.97	1.68	126	64
5	0.56	1.00	158	53

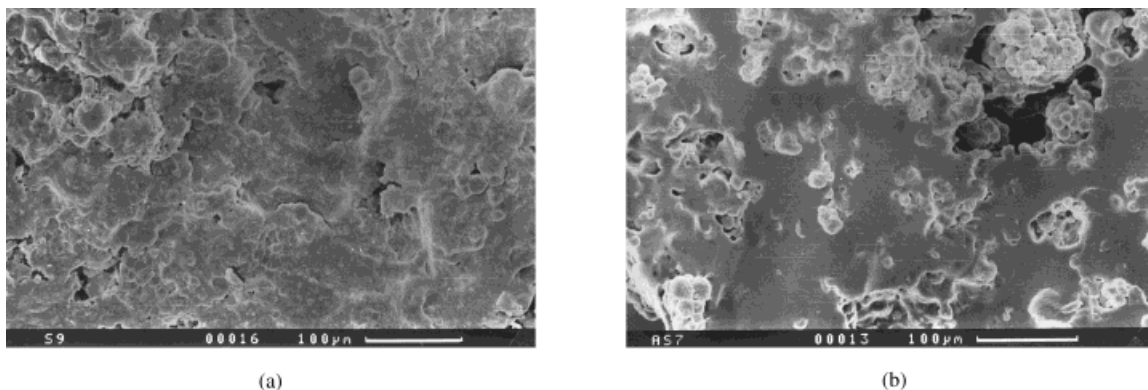
Filler loading: 20 phr; extrusion time: 10 min; extrusion temperature: 150°C; extrusion shear rate: 123 s<sup>-1</sup>.

with increasing filler loading indicates that carbon black facilitates the interaction between PAA and ENR.

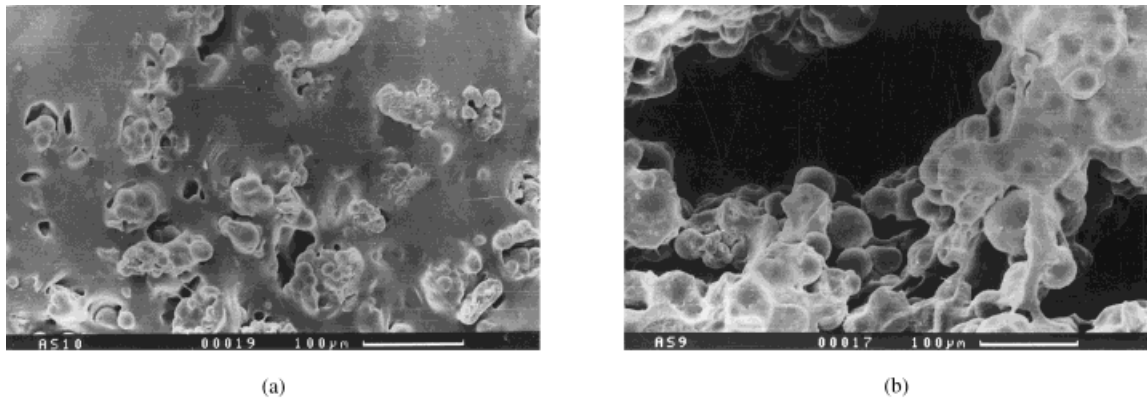
It has been shown in earlier communications that PAA and ENR blend undergoes a chemical interaction during high-temperature molding<sup>1</sup> and carbon black filler actively participates in the initiation of the chemical interaction.<sup>2,3</sup> It is believed that crosslinking between PAA and ENR takes place through free radical mechanism, where chemisorbed PAA chemically reacts with the physisorbed ENR, forming an interfacial crosslinked layer around the filler particles.<sup>4</sup> Thus, incorporation of a free radical acceptor, like thiophenol, is likely to alter the chemorheological behavior of the HAF carbon black filled PAA/ENR blend. The effect of thiophenol concentration on the capillary pressure versus extrusion time plot of 20 phr filled blend is shown in Figure 2. It is evident that the rate of capillary pressure rise decreases with the increase in thiophenol concentration. Figure 4(a) illustrates the effect of thiophenol concentration on the rate of the interaction at a shear rate of 123.0 s<sup>-1</sup> for the 20 phr carbon black filled blend. Figure 4(b) shows that the activation energy of interaction increases with in-

crease in thiophenol concentration. Since network formation during extrusion is believed to take place surrounding the carbon black particles<sup>2-4</sup> by free radical mechanism, thiophenol, as free radical acceptor, deactivates the black surface; as a result, activation energy of interaction during extrusion increases with an increase in thiophenol concentration. The reduction in the extent of interaction in the presence of thiophenol is also evident from stress-strain properties of the extrudates (Table V), which shows that modulus and tensile strength decrease, but elongation at break increases with an increase in thiophenol concentration. Swelling studies of the extrudates reveal that nonextractable ENR decreases with the increase in thiophenol concentration, indicating a lesser extent of interaction between ENR and carbon black.

Figures 5 and 6 show the effect of thiophenol concentration on the SEM photomicrographs of extruded PAA/ENR blend containing 20 phr carbon black, before and after chloroform etching. In the absence of thiophenol, the extrudate shows apparent homogeneity [Fig. 5(a)], which remains unaffected even after chloroform etching [Fig. 5(b)]. Incorporation of thiophenol imparts some



**Figure 5** SEM photomicrographs of the cut surface of the extrudate of PAA-ENR-20 phr HAF carbon black system. Extrusion temperature, 150°C; shear rate, 123 s<sup>-1</sup>; (a) before chloroform etching; (b) after chloroform etching.

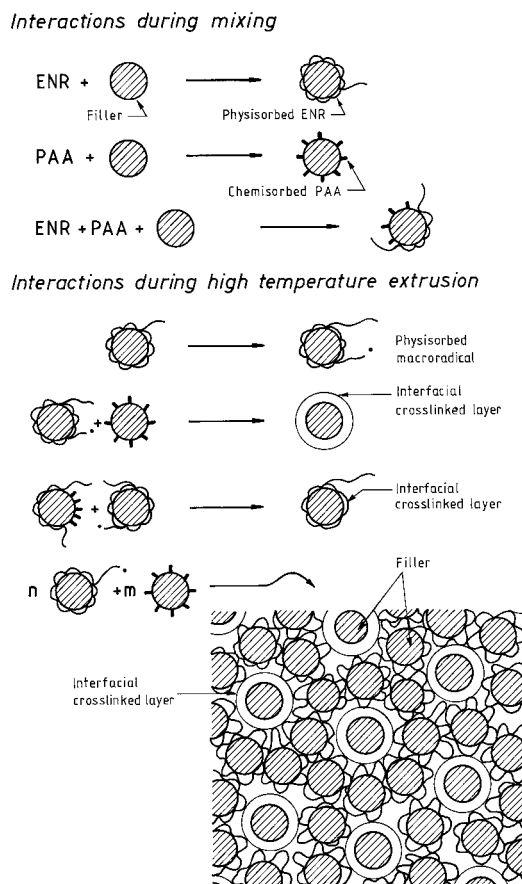


**Figure 6** SEM photomicrographs of the cut surface of the extrudate of PAA-ENR-20 phr HAF carbon black system containing 5 phr thiophenol. Extrusion temperature, 150°C; shear rate, 123 s<sup>-1</sup>; (a) before chloroform etching; (b) after chloroform etching.

degree of heterogeneity [Fig. 6(a)]. Figure 6(b) shows the SEM photomicrograph of chloroform-etched extrudate containing thiophenol. The empty space indicates that the incorporation of thiophenol increases the proportion of solvent-ex-

tractable ENR. This observation leads to the conclusion that the carbon-black-initiated chemical interaction between PAA and ENR is adversely affected in the presence of thiophenol.

Figure 7 suggests a probable mechanism illustrating the role of carbon black in the interaction between PAA and ENR. The mechanism shows that during extrusion, bound ENR generates active physisorbed macroradicals, which react with the chemisorbed PAA to form a filler agglomerate superstructure.<sup>4</sup> It is believed that an increase in temperature, shear rate, or filler loading increases the activity and concentration of the physisorbed macroradicals, facilitating the formation of the agglomerate superstructure and, hence, the increase in capillary pressure. Thiophenol, as free radical acceptor, is sorbed onto the carbon black surface and thus prevents the ENR sorption by carbon black; as a result, the concentration of physisorbed macroradical decreases, suppressing the formation of agglomerate superstructure. This explains why activation energy of interaction in the case of PAA/ENR/carbon black system decreases with an increase in filler loading but increases with an increase in thiophenol concentration.



**Figure 7** Probable mechanism of interaction among PAA, ENR, and carbon black.

## CONCLUSIONS

HAF carbon black filler initiates a chemical interaction between chemisorbed PAA and physisorbed ENR when HAF carbon black filled PAA/ENR blend is extruded through capillary in the MPT. The rate of chemical interaction increases with the increase in filler loading, shear rate, and extrusion time. Presence of a free radical acceptor

like thiophenol causes a reduction in the rate of interaction, giving credence to the proposed free radical mechanism in the carbon-black-initiated interaction between PAA and ENR.

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