Effect of Surface Oxidation of Filler and Silane Coupling Agent on the Chemorheological Behavior of Epoxidized Natural Rubber Filled with ISAF Carbon Black

AJAY K. MANNA,[1] A. K. BHATTACHARYYA,[1] P. P. DE,[1] D. K. TRIPATHY,[1] S. K. DE,[1] DENNIS G. PEIFFER[2]

[1] Rubber Technology Centre, Indian Institute of Technology, Kharagpur, 721302, India

[2] Exxon Research & Engineering Company, Route 22 East, Clinton Township, Annandale, New Jersey 08801

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ABSTRACT: On the basis of results of measurements of physical properties and solvent swelling of the extrudates, it has been observed that epoxidized natural rubber (ENR) interacts chemically with intermediate super abrasion furnace (ISAF) carbon black when the mix of the two was extruded at 130–160°C in a Monsanto Processability Tester (MPT). The extent of interaction between the rubber and filler depends on the following factors: extrusion time, carbon black loading, shear rate, and the extent of oxidation on the carbon black surface. Addition of the silane coupling agent, namely, *N*-3-(-*N*-vinyl benzyl amino) ethyl-γ-amino propyl trimethoxy silane monohydrochloride, enhances the rate of the interaction. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 557–563, 1999

Key words: expoxidizes natural rubber; surface oxidized carbon black; chemorheology; extrusion; silane coupling agent; chemical interaction

INTRODUCTION

It has been reported that during high-temperature molding of rubber–filler mixes, intermediate super abrasion furnace (ISAF) carbon black chemically reacts with epoxidized natural rubber (ENR), and the effect is more prominent in the case of oxidized ISAF grade of black and in the presence of the silane coupling agent, namely, *N*-3-(*N*-vinyl benzyl amino) ethyl-γ-aminopropyl trimethoxy silane monohydrochloride.[1,2]

The rheological behavior of carbon black filled systems has been studied by several workers.[3–8] The effects of the state of cure on the rheological behavior of thermosets have also been reported.[9–15] Mallick et al. studied the effect of carbon black on the chemorheological behavior of blends of polyacrylic acid (PAA) and epoxidized natural rubber in a Monsanto Prossability Tester (MPT).[16] The rheological behavior of SBR compounds affected by vulcanization kinetics was studied by Isayev and Wan[17] and Wan and Isayev.[18] Recently, Bandyopadhyay et al. studied the effect of silane coupling agent, namely, (3-aminopropyl) trimethoxy silane, on the chemorheological behavior of a mixture of carboxylated nitrile rubber (XNBR) and surface-oxidized ISAF carbon black.[19]

The present article reports the results of studies on the effect of surface oxidation of ISAF carbon black on the chemorheological behavior of ENR, with special reference to the effect of silane coupling agent, namely, *N*-3-(*N*-vinyl benzyl amino) ethyl-γ-aminopropyl trimethoxy silane monohydrochloride.

EXPERIMENTAL

The details of the materials used are given in Table I, and the formulations of the mixes are

Correspondence to: S. K. De.

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Table I Details of Materials Used

Materials	Characteristics	Source
Epoxidized natural rubber (ENR)	50 mol % of the double bonds are epoxidized	Kumpulan Guthrie Berhad, Malaysia
Intermediate super abrasion furnace (ISAF) carbon black	DBP,[a] 45 cm^3/100 g; N_2SA,[b] 105 m^2/g; pH 9.5; % O_2,[c] 0.9	Degussa AG, Germany
Surface oxidized intermediate super abrasion furnace (ox-ISAF) carbon black	DBP,[a] 47 cm^3/100 g; N_2SA,[b] 105 m^2/g; pH 2.8; % O_2,[c] 1.4	Degussa AG, Germany
Silane coupling agent, *N*-3-(*N*-vinyl benzyl amino) ethyl-γ-amino propyl trimethoxy silane monohydrochloride (Trade name, Z-6032)	Specific gravity, 0.9 at 25°C; pH 2.0	Dow Corning, U.S.A.

[a] Dibutyl phthalate absorption value.
[b] Nitrogen surface area.
[c] Percent oxygen content.

given in Tables II and III. The mixing of the rubber, filler, and silane coupling agent was carried out in a Brabender Plasticorder (PLE 330) at room temperature (25°C) at a rotor speed of 60 rpm. First, carbon black was mixed with ENR for 4 min, then silane coupling agent was added dropwise, and the mixing was continued further for 4 min. The mixes were then taken out from the Brabender Plasticorder, and final sheeting was done in a two-roll mill.

The flow properties of the rubber–filler mixes were measured in a Monsanto Processability Tester (MPT, model 83077), which is a constant flow rate capillary rheometer that can be operated manually or in a programmed way. The barrel, piston, and capillary all are electrically heated with a microprocessor-based temperature controller system. The capillary used for extrusion of the rubber compounds has a L/D ratio of 30 : 1, with compound entrance angles of 45 and 60°. The barrel and capillary diameters were 19.06 and 1.00 mm, respectively. The preheating time for all the samples was 5 min, and the change in shear rates was achieved by changing the plunger speed. During extrusion, the plot of the capillary pressure against time was automatically recorded in a graph by a plotter. For extrusion of the mixes without coupling agent, the temperatures were 160, 170, and 180°C. For samples containing coupling agent, extrusion was carried out at 140, 150, and 160°C. The effects of shear rates on the chemical interaction between rubber and carbon black was studied at 130°C at 100 phr of carbon black loading.

The solvent swelling of the extrudates was done in chloroform for 72 h at 25°C, and the final weight was taken under swollen conditions. The results are expressed as the percentage of volume swell. The physical properties of the extrudates were determined in a Zwick Universal Testing Machine (UTM), model-1435, at room temperature (25°C), with the rate of grip separation being 500 mm/min. The area of cross section of the extrudates were calculated from the average diameter of the extrudates.

RESULTS AND DISCUSSION

Plots of the increment in the capillary pressure (ΔP) versus extrusion time (t) for various ENR–carbon black mixes are shown in Figure 1. It was

Table II Formulations of Mixes of ENR and Carbon Black

Materials	Mix Designation					
	EI_6	EI_8	EI_{10}	EO_6	EO_8	EO_{10}
ENR	100	100	100	100	100	100
ISAF carbon black	60	80	100	0	0	0
Oxidized ISAF carbon black	0	0	0	60	80	100

Table III Formulations of Mixes of ENR and Carbon Black in the Presence of the Silane Coupling Agent

Materials	Mix Designation						
	EZ_4	EI_6Z_2	EI_6Z_4	EI_6Z_6	EO_6Z_2	EO_6Z_4	EO_6Z_6
ENR	100	100	100	100	100	100	100
ISAF carbon black	0	60	60	60	0	0	0
Oxidized ISAF carbon black	0	0	0	0	60	60	60
Coupling agent Z-6032	4	2	4	6	2	4	6

observed that ΔP increases with an increase in extrusion time, and the rate of increase in ΔP is higher at a higher loading of carbon black. Furthermore, the effect is more pronounced in the case of the oxidized grade of carbon black. Neat ENR, however, does not show any such increment in ΔP with extrusion time, indicating that the increment in capillary pressure with extrusion time in the case of rubber–carbon black mixture is due to the chemical bonding between the surface groups of the filler and the active sites of the rubber. It is evident that the extent of chemical interaction increases on the surface oxidation of carbon black. As the surface-oxidized ISAF carbon black contains both —COOH (benzoic) and —OH (phenolic) groups,[1] a greater extent of chemical interaction takes place in the case of oxidized grade of carbon black as compared to the nonoxidized grade, which contains only phenolic —OH groups.[1]

The effect of shear rate on the increment of capillary pressure (ΔP) at a constant temperature (130°C) at 100 phr filler loading is shown in Figure 2. The results clearly indicate that the rate of chemical interaction increases with increase in shear rate, and the effect is more prominent in the case of oxidized grade of carbon black.

Figure 3 shows the plots of increment in the capillary pressure (ΔP) as a function of the silane coupling agent. In the case of the oxidized grade of carbon black, the increment in capillary pressure (ΔP) is highest at the coupling agent loading of 4 phr, beyond which ΔP decreases, presumably due to the plasticizing action of the excess cou-

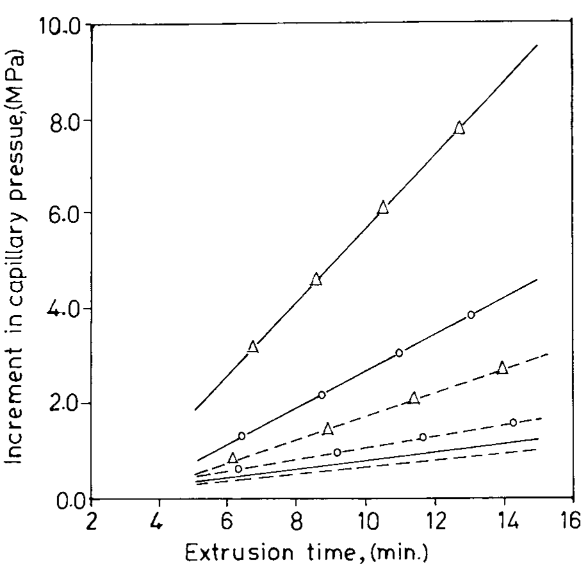

Figure 1 Plots of increment in capillary pressure with time for ENR-carbon black mixes at 140°C and at a shear rate of 24.3 s^{-1}: (—) EO_6, (–○–) EO_8, (–△–) EO_{10}, (----) EI_6, (--○--) EI_8, (--△--) EI_{10}.

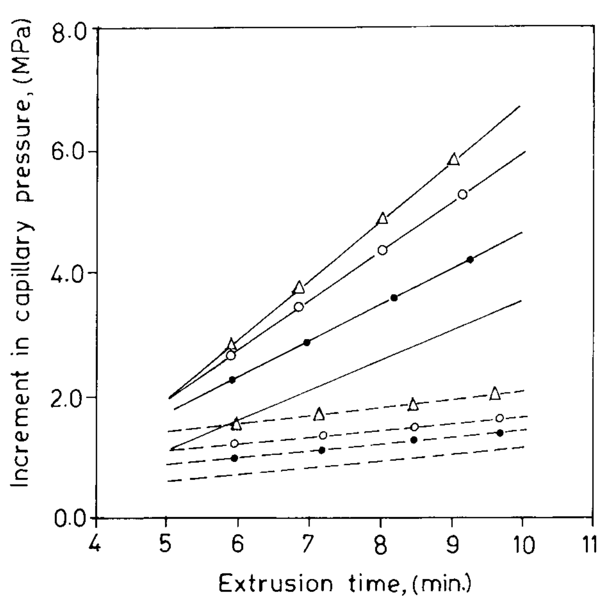

Figure 2 Plots of increment in capillary pressure with time for ENR-carbon black mixes at different shear rates: (—) EO_{10} and (---) EI_{10}, 12.2 s^{-1}; (–•–) EO_{10} and (--•--) EI_{10}, 24.3 s^{-1}; (–○–) EO_{10} and (--○--) EI_{10}, 49.2 s^{-1}; (–△–) EO_{10} and (--△--) EI_{10} 98.3 s^{-1}.

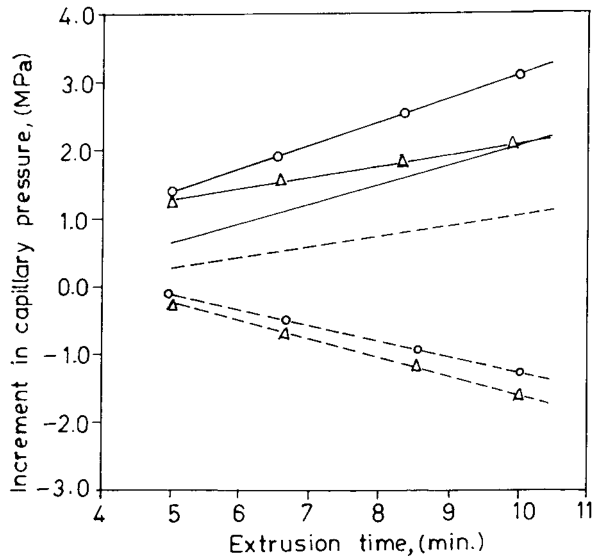

Figure 3 Plots of increment in capillary pressure with time for ENR–carbon black mixes in the presence of coupling agent at 150°C and at a shear rate of 24.3 s^{-1}: (——) EO_6Z_2, (–○–) EO_6Z_4, (–△–) EO_6Z_6, (---) EI_6Z_2, (--○--) EI_6Z_4, and (--△--) EI_6Z_6.

pling agent that migrates on to the surface of the capillary wall and leads to wall slippage. In the case of ISAF carbon black, however, the rise in ΔP attains a maximum at the coupling agent loading of 2 phr. It has been reported earlier that the surface-oxidized carbon black contains a greater number of reactive functional groups, as compared to the nonoxidized grade, which can react with the active sites of coupling agent. Accordingly, the optimum loading of the silane coupling agent is greater in the case of the oxidized grade of carbon black.

Tables IV and V summarize the effects of filler loading, extrusion time, shear rate, and the coupling agent loading on the mechanical properties of the extrudates. It is observed that tensile strength and modulus of the extrudates increase with an increase in extrusion time and shear rate, and the effect is more pronounced in the case of the oxidized grade of carbon black and in the presence of the coupling agent.

Figure 4 shows that the volume swell decreases with an increase in the shear rate in all the cases, signifying that the extent of the chemical interaction increases with shear rate. The effect is more pronounced in the case of the oxidized grade of carbon black and in the presence of the coupling agent.

The chemorheology of a mix is influenced by the reaction kinetics of the system.[11,12] The linear rise in the capillary pressure with extrusion time, as shown in Figures 1–3, can be expressed as

$$d(\Delta P)/dt = \mathrm{m} \tag{1}$$

where ΔP is the increment in the capillary pressure at any time t, and m is a constant for a particular formulation, at a particular temperature and obtained from the slope in Figures 1–3. Since the increment in the capillary pressure is

Table V Effect of Shear Rate on the Tensile Strength (MPa) of Extrudates

	Mix Designation			
Shear Rate (s^{-1})	EO_6 (EI_6)	EO_8 (EI_8)	EO_{10} (EI_{10})	EOZ_2 (EIZ_2)
24.3	5.1 (3.2)[a]	5.8 (3.6)	6.2 (4.0)	6.3 (4.2)
49.2	5.8 (3.5)	6.4 (4.0)	7.1 (4.3)	6.8 (4.8)
98.3	6.3 (3.9)	6.9 (4.3)	7.8 (4.5)	7.5 (5.2)

Extrusion done at 150°C; extrudates collected after 10 min.
[a] The values in the parentheses indicate the results of ISAF carbon black filled samples.

Table IV Effect of Extrusion Time on the Mechanical Properties of Extrudates

	Extrusion Time: EI_{10} (min)			Extrusion Time: EO_{10} (min)		
Mix Designation	5	10	15	5	10	15
Tensile strength (MPa)	3.2	4.0	4.8	6.2	7.5	8.3
Modulus at 100% elongation (MPa)	1.1	1.2	1.3	3.0	3.3	3.5
Elongation at break (%)	730	710	700	270	260	255

The extrusion temperature is 150°C, and the shear rate is 24.3 s^{-1}.

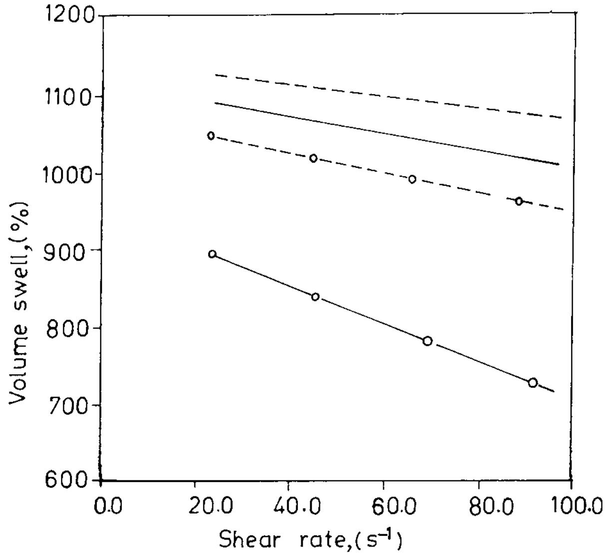

Figure 4 Effect of the shear rate on the solvent swelling of extrudates. The following extrudates were collected after 10 min: (——) EO_6; (–○–) EO_6Z_2; (---) EI_6; (--○--) EI_6Z_2.

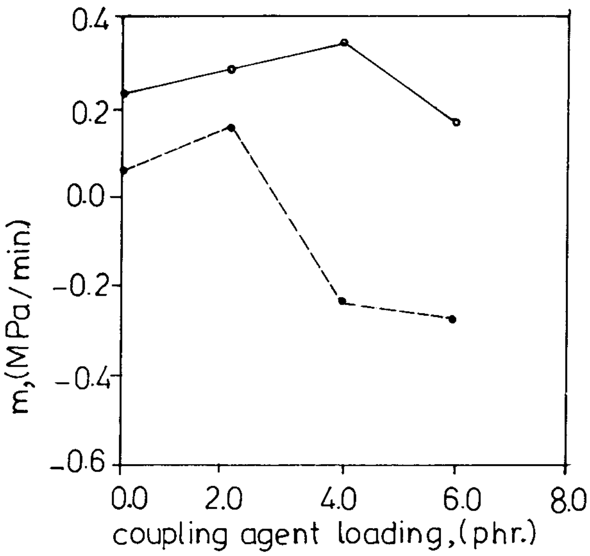

Figure 6 Effect of coupling agent loading on m at 150°C and at a shear rate of 24.3 s^{-1}: (–○–) oxidized ISAF carbon black; (--●--) ISAF carbon black.

due to enhanced viscosity through rubber–filler interaction, m can be considered as proportional to the rate of the rubber–filler interaction.

Figure 5 shows the variation of m with volume fraction of filler at constant temperature and shear rate. It is observed that m increases with increase in filler loading and on oxidation of the carbon black surface.

Figure 6 shows the variation of m with the loading of silane coupling agent at constant filler loading. It is evident that m is higher in the case of oxidized ISAF carbon black, and it passes through a maximum at a coupling agent loading

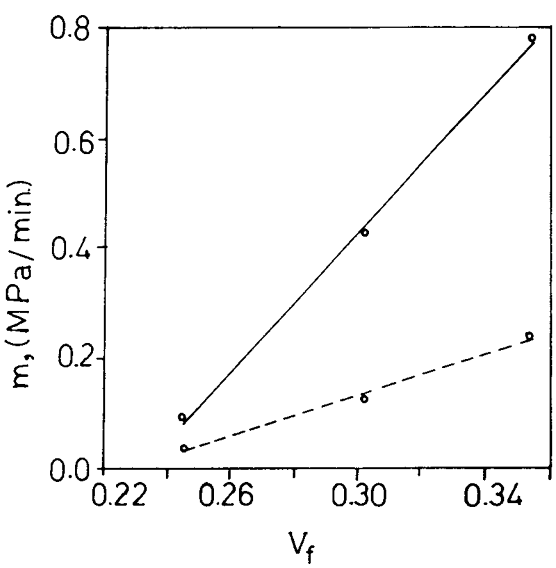

Figure 5 Variation of m with volume fraction (V_f) of carbon black: (——) oxidized ISAF carbon black; (---) ISAF carbon black.

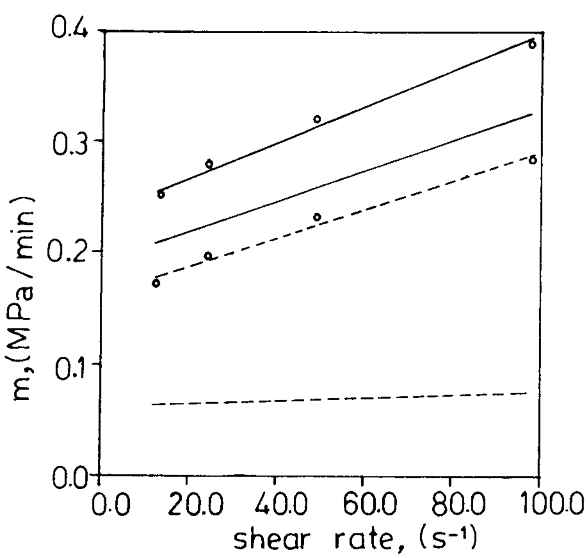

Figure 7 Variation of m with shear rate at 150°C: (——) EO_6; (–○–) EO_6Z_2; (---) EI_6; (--○--) EI_6Z_2.

of 4 phr; while in the case of the nonoxidized grade of the filler, the maximum occurs at a loading of 2 phr. The decrease of m at higher loading of the coupling agent is possibly due to migration of the coupling agent on to the capillary wall and causes wall slippage, which, in turn, causes a drop in the increment in barrel pressure.

Figure 7 shows the effect of shear rate on m. It is observed that m increases with an increase in shear rate, and the effect is more prominent in the case of the oxidized grade of carbon black and in the presence of the silane coupling agent. It is likely that the viscous heating during extrusion of the highly filled system is responsible for the observed dependence of m on shear rate.

Figures 8 and 9 suggest a probable mechanism of the chemical interaction between ENR and ISAF carbon black, illustrating the role of coupling agent in the chemical interaction. It has been proposed earlier that during high-temperature molding of the rubber–filler mixture, the —OH and —COOH groups on the filler surface react with the —OCH_3 group of the coupling agent, while —NH_2^+— reacts with the epoxy groups of ENR, leading to formation of the coupling bonds.[1,2] Figures 8 and 9 illustrate probable mechanism of bonding between the rubber and the filler and the role of the coupling agent in the rubber–filler bonding.

CONCLUSIONS

ENR and ISAF carbon black interact chemically with each other when the mixture of the two is extruded in a Monsanto Processability Tester. The extent of the interaction increases upon surface oxidation of carbon black, an increase in shear rate, and the addition of the silane coupling agent, namely, *N*-3-(*N*-vinyl benzyl amino) ethyl-γ-aminopropyl trimethoxy silane monohydrochloride.

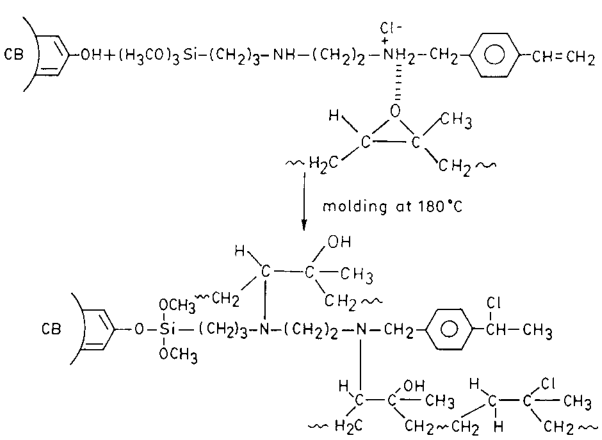

Figure 8 Proposed mechanism of reaction between ENR and ISAF black in the presence of the silane coupling agent.

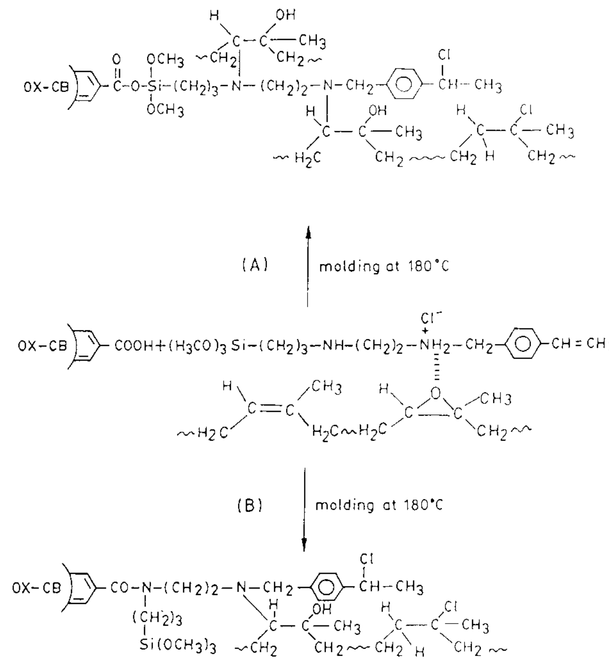

Figure 9 Proposed reaction mechanism between ENR and oxidized ISAF black in the presence of the silane coupling agent.

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