Effect of (3-Aminopropyl) Triethoxysilane on Chemorheological Behavior of Carboxylated Nitrile Rubber in Presence of Surface Oxidized ISAF Carbon Black

SUMANDA BANDYOPADHYAY, P. P. DE, D. K. TRIPATHY, S. K. DE

Rubber Technology Centre, Indian Institute of Technology, Kharagpur 721 302, India

Received 13 February 1996; accepted 28 August 1996

ABSTRACT: Carboxylated nitrile rubber and ISAF carbon black chemically interacted when the mix of the two was extruded at high temperature (180°C) in a Monsanto Processibility Tester. Studies on the physical properties of the extrudates and the reaction kinetics of the extrusion process showed that the extent of interaction increased with increase in filler loading, oxygen-containing functional groups on the filler surface, shear rate, extrusion time, and the loading of (3-aminopropyl) triethoxysilane. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **63:** 1833–1839, 1997

INTRODUCTION

It has been reported that during high-temperature molding, surface oxidized furnace blacks chemically interact with carboxylated nitrile rubber (XNBR)[1] and the extent of interaction increases in presence of (3-aminopropyl) triethoxysilane (APTS).[2] The present paper reports the results of the processibility studies of the XNBR–carbon black mixes in a Monsanto Processibility Tester (MPT) with special reference to the effect of surface oxidation of ISAF carbon black filler and incorporation of APTS.

Although rheological behavior of carbon black-filled elastomers have been studied extensively,[3–9] little is reported on the processibility of the surface-oxidized carbon black-filled elastomers. The chemorheological behavior of thermosetting resins have been studied by various researchers.[10–15] Recently, Mallick et al. have studied the effect of carbon black on the processibility of the blends of polyacrylic acid (PAA) and epoxidized natural rubber (ENR) in MPT.[16]

Correspondence to: S. K. De.

Contract grant sponsor: Council of Scientific and Industrial Research, Government of India, New Delhi.

EXPERIMENTAL

Preparation of the Mixes

Details of the materials used are given in Table I and the formulations of the different mixes are shown in Table II. Mixing of the carbon black, APTS, and XNBR was done in a Brabender Plasticorder (PLE 330) at room temperature using a rotor speed of 60 rpm. APTS was added dropwise to the carbon black–XNBR mix and the duration of the mixing cycle was 8 min. The mix was then taken out from the Brabender Plasticorder and the final sheeting was done in a two-roll mill.

Rheological Properties

The flow properties of the compounds were measured in a Monsanto Processibility Tester (MPT), which is a fully automatic high pressure capillary viscometer. The barrel and capillary are electrically heated with a microprocessor-based temperature controller system. The instrument details are available from the literature.[17,18] The capillary used was of length to diameter ratio 20 : 1, having a multiple cone entry with compound entrance angle of 45° and 60°. The barrel and capillary diameters were 19.06 mm and 1 mm, respectively.

Table I Details of Materials Used

Material	Characteristics	Source
Carboxylated nitrile rubber (XNBR) KRYNACK X 7.50	% acrylonitrile = 27 % carboxyl = 7 Mooney viscosity (ML1 + 4 at 100°C), 50	Bayer Polysar, France
Oxidized ISAF black (Spezialschwarz-550)	DBP: 47 cc/100 gm N_2SA: 110 m^2/gm pH: 2.8, %O_2: 1.44	Degussa AG, Germany
ISAF black (Printex-55)	DBP: 45 cc/100 gm N_2SA: 105 m^2/gm pH; 9.5, %O_2: 0.9	Degussa AG, Germany
Coupling agent, 3-aminopropyl triethoxy silane	Specific gravity: 0.942 gm/cc Boiling point: 217°C	Fluka Chemical Corporation, U.S.A.

The pre-heating time for the samples were constant at 3 min at the extrusion temperature. The change in the shear rate was achieved by changing the plunger speed. During extrusion, the plot of capillary pressure against time was automatically made on a plotter. For calculating the activation energy, extrusion was done at different temperatures. For mixes without APTS, temperatures were 160°, 170°, and 180°C. The mix XOB_1 (Table I) was also extruded at 140°C. For the mixes containing APTS, the temperatures were 120°, 130°, and 140°C since the extrusions were not smooth at temperatures exceeding 150°C.

Solvent Swelling

The solvent swelling of the extrudates was done in chloroform. The extrudates were allowed to swell for 72 h to attain equilibrium swelling at room temperature and then taken out and vacuum dried to constant weight. The results of solvent swelling experiments were expressed as the percentage weight loss of rubber on swelling.

Physical Properties

The physical properties of the extrudates were determined in a Zwick UTM model 1435 at room temperature, the rate of grip separation being 500 mm/min. The area of cross-section of the extrudates were calculated from the diameter of the extrudates.

RESULTS AND DISCUSSION

Plots of the increment in capillary pressure versus extrusion time for various XNBR-carbon black mixes are shown in Figure 1. It is observed that the increment in capillary pressure (ΔP) increases with extrusion time and the rate of increase in pressure increment is higher at higher loadings of carbon black. Furthermore, the effect is more prominent in the case of oxidized ISAF carbon black. Neat XNBR, however, does not show any increment in pressure with extrusion time. It was also noted that the NBR-oxidized ISAF carbon black system also shows a negligible increment in the capillary pressure with extrusion time. Therefore, it can be argued that the increment in pressure with extrusion time in the case of XNBR-oxidized ISAF carbon black mixes is due to chemical interaction between the —COOH groups of XNBR and the —OH groups of the ISAF

Table II Details of the Formulations Used

Material	Mix Designation								
	XOB_1	XOB_2	XOB_3	XB_1	XB_2	XB_3	XOB_{11}	XOB_{12}	XOB_{13}
XNBR	100	100	100	100	100	100	100	100	100
ISAF	—	—	—	75	85	100	—	—	—
Oxidized ISAF	75	85	100	—	—	—	75	75	75
APTS	—	—	—	—	—	—	1.8	3.75	7.5

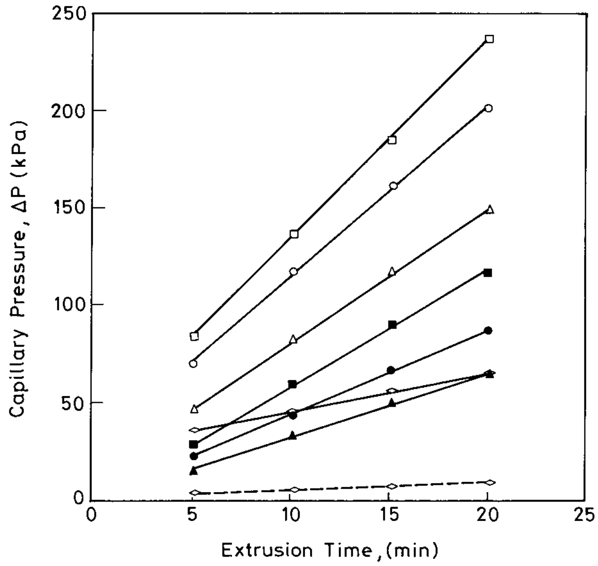

Figure 1 Plots of increment in capillary pressure with time for XNBR–carbon black systems (– △ –), 75 phr; (– ○ –), 85 phr; (– □ –), 100 phr. The hollow captions are for XNBR-oxidized ISAF black system and the filled captions are for XNBR-ISAF black system. (——), NBR-75 phr oxidized ISAF carbon black and (– – –), neat XNBR. Extrusion temperature 180°C and shear rate 61.54 cm^{-1}.

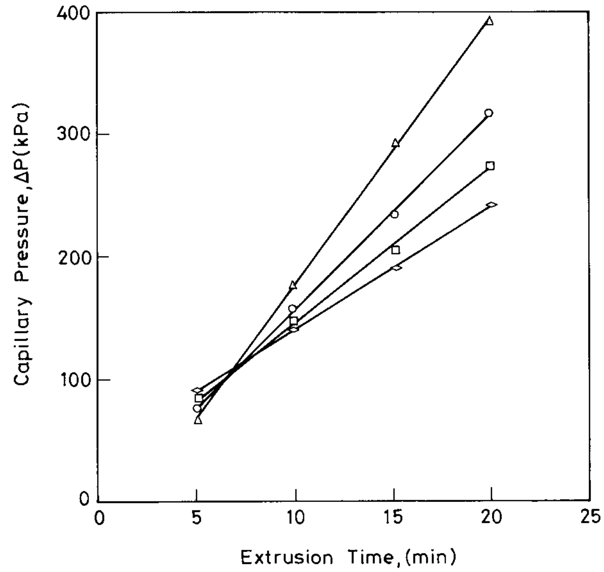

Figure 3 Plots of increment in capillary pressure with time for XNBR–carbon black systems in presence of APTS; (– ◇ –), 0 phr; (– □ –), 1.8 phr; (– ○ –), 3.75 phr; (– △ –), 7.5 phr. Extrusion temperature, 140°C and shear rate, 61.54 s^{-1}.

black. Similar interaction has been proposed in the case of high temperature molding of XNBR-oxidized ISAF black mixes.[1] Figure 2 shows the effect of shear rate on the increment of capillary pressure in the system containing 75 phr of oxidized ISAF black. It is seen that the rate of increase in the increment of capillary pressure is higher as the shear rate increases. Figure 3 shows the plot of increment in capillary pressure with extrusion time for the formulations containing different loadings of APTS. The capillary pressure increment is higher as the loading of APTS increases. It has been reported earlier that APTS acts as a promoter for chemical interaction between XNBR and ISAF carbon black.[2] APTS is known to play a dual role in the XNBR-oxidized ISAF carbon black system. First, it reduces the viscosity of the matrix by reducing the extent of filler–filler interaggregate formation and secondly, it enhances the degree of crosslinking of the matrix by increasing the rubber–filler bonding.[19] The effect of APTS on the rheological behavior is evident from Figure 3. It is seen that increasing loading of APTS causes lowering of the capillary pressure of the matrix in the initial stages of extrusion, but at longer extrusion times APTS causes increase in capillary pressure due to the crosslinking of the rubber phase by the active sites of the filler.

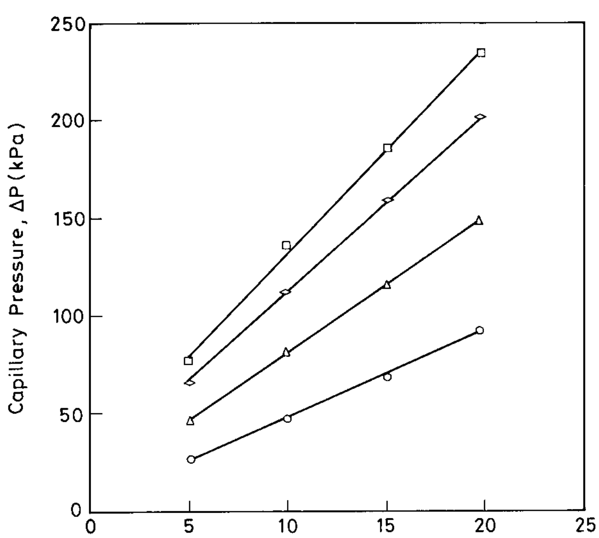

Figure 2 Plots of increment in capillary pressure with time for XNBR-carbon black systems at different shear rates; (– ○ –), 24.6 s^{-1}; (– △ –), 61.54 s^{-1}; (– ◇ –), 94.5 s^{-1}; (– □ –), 123.08 s^{-1}. Extrusion temperature, 180°C.

Tables III–VI summarize the effects of filler loading, shear rate, extrusion time, and APTS

Table III Effect of Filler Loading on the Physical Properties of the Extrudates: Extrudate Shear Rate, 61.54 s^{-1} and Extrusion Temperature, 180°C

Properties	Mix Designation					
	XOB_1	XOB_2	XOB_3	XB_1	XB_2	XB_3
100% Modulus (MPa)	2.3	3.0	3.4	1.6	1.7	1.7
Tensile strength (MPa)	5.3	6.4	7.2	1.7	2.5	3.2
Elongation at break (%)	374	259	200	480	450	400
% wt loss on swelling	50	44	30	70	61	45

loading on the physical properties of the extrudates. While modulus and tensile strength increase, the elongation at break decreases with filler loading, the effect being more prominent in the case of oxidized grade of ISAF carbon black. It was also observed that increase in shear rate and extrusion time causes improvement in physical properties of XNBR-oxidized ISAF black. Furthermore, physical properties register manyfold increase in the presence of APTS. Percentage swelling can be related to the extent of crosslinking in the sense that the lower weight loss infers a higher extent of crosslinking. Accordingly, it is believed that extrusion in MPT causes crosslinking in XNBR by oxygen-containing groups of carbon black and the extent of crosslinking increases with filler loading, shear rate, extrusion time, and surface oxidation of carbon black.

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

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

where ΔP is the increment in capillary pressure at any time t; m being a constant for a particular formulation and is obtained from the slope in the plots in Figures 1–3. Since the increment in capillary pressure is due to enhanced rubber–filler interaction, therefore following Lodge,[20] it can be stated that,

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

where, C_α is the extent of interaction, R is the universal gas constant, and T is the absolute temperature. From eq. (1) and (2) it can be stated that,

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

where dC_α/dt is the rate of interaction. In the present system, the concentration of the functional groups or the active sites in the rubber is sufficiently high and is taken as constant, making the rate of interaction independent of the concentration of the active sites of the rubber. Therefore, the rate of the interaction is dependent only on the concentration of the active sites on the carbon black for mixes not containing APTS or on the loading of APTS at fixed filler loading, as the case may be. Hence the process follows pseudo-unimo-

Table IV Effect of Shear Rate on the Physical Properties of the Extrudates of XOB_1: Extrusion Temperature, 180°, and Extrusion Time, 10 min

Shear Rate (γ)	100% Modulus (MPa)	Tensile Strength (MPa)	Elongation at Break (%)	% Wt Loss on Swelling
24.6	2.0	3.9	953	58
61.54	2.3	5.3	374	50
94.5	3.0	6.2	180	46
123.08	3.4	7.4	154	40

Table V Effect of Extrusion Time on the Physical Properties of the Extrudates of XOB_3: Extrusion Temperature, 180°C, and Shear Rate, 61.54 s^{-1}

Run Time (min)	100% Modulus (MPa)	Tensile Strength (MPa)	Elongation at Break (%)	% Wt Loss on Swelling
5	1.2	3.9	410	80
10	1.5	4.5	350	69
15	2.8	5.9	275	57
20	3.4	7.2	200	50

lecular rate equation which in the present case is defined as,

$$m/RT = kC \quad (4)$$

where k is the rate constant of the rubber–filler interaction and C is the concentration of either the active sites on the filler or the APTS.

In the case of neat XNBR and NBR-oxidized ISAF carbon black system, the activation energy is assumed to be very high, which precludes the chemical interaction during extrusion. The presence of the —COOH groups in XNBR and the functional groups in oxidized ISAF black reduces the activation energy of the chemical interaction and hence the rate constant of the interaction increases. Figure 4 shows the variation of rate of interaction with volume fraction of filler at constant shear rate for three different temperatures. Here, it is assumed that increase in volume fraction of filler increases the concentration of active sites of the filler. Figure 5 shows the variation of rate of interaction with shear rate at constant volume fraction of filler and temperature. Figure 6 shows the variation of rate of interaction with APTS loading at constant volume fraction of filler and shear rate. It is observed from Figures 4–6 that the rate of interaction increases with filler loading and the increase is more prominent in case of oxidized ISAF black and at higher shear rate and in presence of APTS. The rate constant k is obtained from the slope of the straight lines in Figures 4–6. Activation energy of the interaction is determined by using the Arrhenius equation,

$$k = A_0 e^{-E_a/RT} \quad (5)$$

where A_0 is the frequency factor and E_a is the energy of activation. The above relation is valid only for homogeneous reactions and in the present heterogeneous system it can be used as an empirical relationship. Therefore, a plot of ln k versus $1/T$ (Fig. 7) would give $-E_a/R$ as the slope of the straight line. Table VII summarizes the values of activation energy for the different compositions. It is seen that the system with oxidized ISAF black system has lower activation energy than the system with ISAF grade of carbon black, and the system containing APTS having the lowest activation energy. It is, therefore,

Table VI Effect of APTS Loading on the Physical Properties of the Extrudates: Extrusion Temperature, 140°C, and Shear Rate, 61.54 s^{-1}

	Mix Designation			
Properties	XOB_1	XOB_{11}	XOB_{12}	XOB_{13}
100% modulus (MPa)	—[a]	2.9	3.4	3.6
Tensile strength (MPa)	—[a]	9.5	11.8	13.9
Elongation at break (%)	—[a]	298	274	250
% wt loss on swelling	—[a]	35	24	18

[a] Could not be determined.

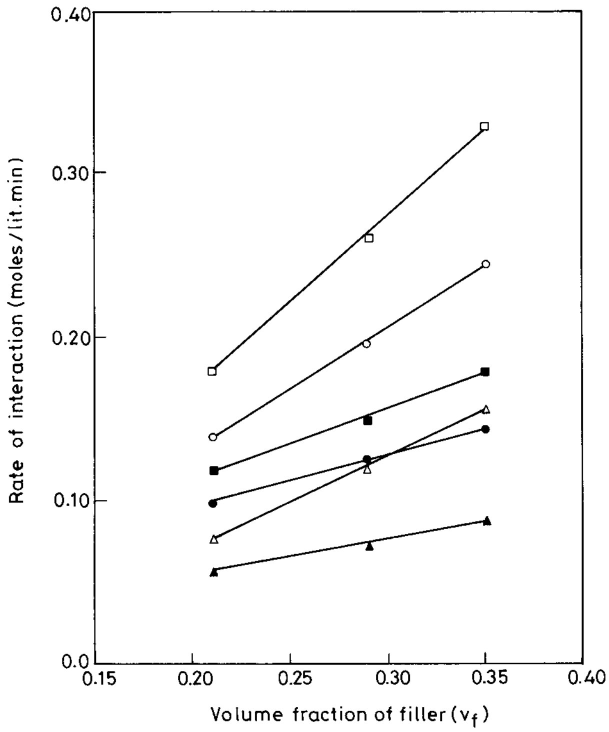

Figure 4 Variation of the rate of interaction with volume fraction of filler for the XNBR–carbon black systems, (– □ –), 180°C; (– ○ –), 170°C; (– △ –), 160°C. The hollow captions are for XNBR-oxidized ISAF black system and the filled captions are for XNBR–ISAF black system.

confirmed that increased oxygen containing functional groups facilitate the chemical interaction between XNBR and carbon black and APTS accelerates the chemical interaction between XNBR and oxidized ISAF carbon black.

Figure 8 suggests a probable scheme of chemical interaction between XNBR and ISAF carbon

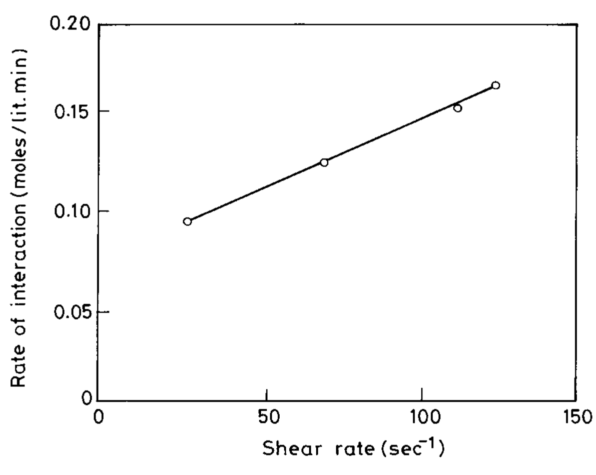

Figure 5 Variation of rate of interaction with shear rate for the XNBR-oxidized ISAF black system containing 75 phr of the black.

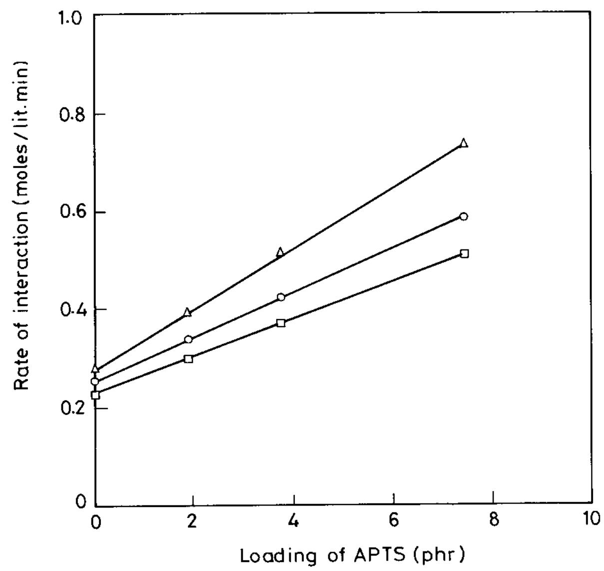

Figure 6 Variation of rate of interaction with loading of APTS for the XNBR-oxidized ISAF black with 75 phr of the black; (– △ –), 140°C; (– ○ –), 130°C; (– □ –), 120°C.

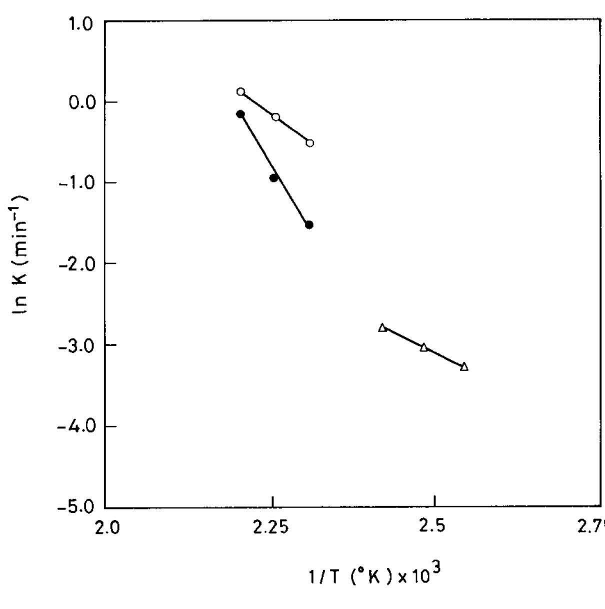

Figure 7 Plot of ln k versus $1/T$ for (– ○ –), XNBR-oxidized ISAF black; (– ● –), XNBR–ISAF black; (– △ –), XNBR-oxidized ISAF black-APTS.

Table VII The Activation Energies of Chemical Interaction for the Different XNBR–Carbon Black Systems

	XNBR + ISAF Black	XNBR + Oxidized ISAF Black	XNBR + APTS + Oxidized ISAF Black
Activation energy (KJ/mol)	166.4	74.8	51.2

black, illustrating the role of APTS in the interaction. It is proposed that during high-temperature extrusion, —OH groups of the filler surface react with the —COOH groups of XNBR. In the presence of APTS, the amino and the ethoxy groups of the APTS react with the —COOH groups of XNBR and the —OH groups of the filler, respectively, to form a tight network.

CONCLUSION

XNBR and ISAF carbon black chemically interact when extruded in MPT at high temperature. The extent of interaction increases with filler loading, oxygen-containing functional groups, shear rate, extrusion time, and APTS loading.

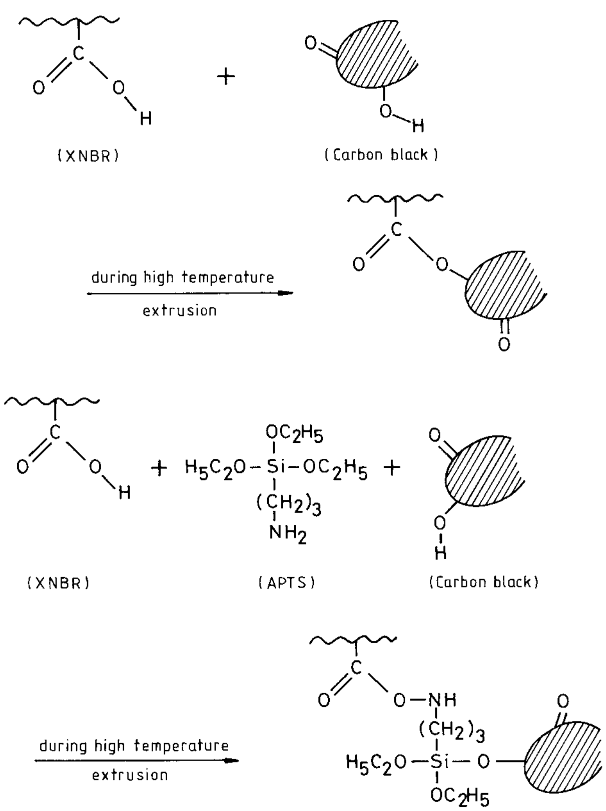

Figure 8 Schematic presentation of the interaction between XNBR carbon black and APTS.

REFERENCES

1. S. Bandyopadhyay, P. P. De, D. K. Tripathy, and S. K. De, *J. Appl. Polym. Sci.,* **58,** 719 (1995).
2. S. Bandyopadhyay, P. P. De, D. K. Tripathy, and S. K. De, *Rubber Chem. Technol.,* to appear.
3. J. R. Hopper, *Rubber Chem. Technol.,* **40,** 463 (1967).
4. J. L. White and J. W. Crowder, *J. Appl. Polym. Sci.,* **18,** 1013 (1974).
5. S. D. Rong and C. E. Chaffey, *Rheol. Acta,* **27,** 179 (1988).
6. K. C. Shin, J. L. White, R. Brzoskowski, and N. Nakajima, *Rubber Chem. Technol.,* **43,** 181 (1990).
7. B. Fajdiga and Z. Susteric, *Kautsch. Gummi Kunstst.,* **46,** 225 (1993).
8. K. C. Shin and J. L. White, *Rubber Chem. Technol.,* **66,** 121 (1993).
9. I. Soos, *Kautsch. Gummi Kunstst.,* **47,** 502 (1994).
10. K. W. Lem and C. D. Han, *J. Appl. Polym. Sci.,* **28,** 3207 (1983).
11. D. S. Lee and C. D. Han, *Polym. Eng. Sci.,* **27,** 964 (1987).
12. D. S. Lee and C. D. Han, *J. Appl. Polym. Sci.,* **34,** 1235 (1987).
13. T. H. Hou, J. Y. Z. Huang, and J. A. Hinkley, *J. Appl. Polym. Sci.,* **41,** 819 (1990).
14. M. S. Lin and R. J. Chang, *J. Appl. Polym. Sci.,* **46,** 815 (1992).
15. D. J. Burlett and J. T. Lindt, *Rubber Chem. Technol.,* **66,** 411 (1993).
16. A. Mallick, A. K. Bhattacharya, D. K. Tripathy, and S. K. De, *J. Appl. Polym. Sci.,* to appear.
17. E. R. Roger, R. J. Baker, and G. L. Hanna, paper presented at the 10th meeting of the Rubber Division, ACS, San Francisco, California, 4–8 October, 1976.
18. *Monsanto Processibility Tester,* Operation and Service Manual, Monsanto Company.
19. S. Bandyopadhyay, P. P. De, D. K. Tripathy, and S. K. De, *J. Appl. Polym. Sci.,* **61,** 1813 (1996).
20. A. S. Lodge, *Trans. Faraday Soc.,* **52,** 120 (1956).