

3-Aminopropyltriethoxysilane as a Promoter in the Crosslinking of Carboxylated Nitrile Rubber by Surface-Oxidized Carbon Black

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

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

SYNOPSIS

The role of aminopropyltriethoxysilane in the interaction between ISAF carbon black and carboxylated nitrile rubber was studied by measurements of bound rubber, physical and dynamic mechanical properties of the vulcanizates, and Monsanto Rheometric studies on the rubber-filler mixes. It is believed that —NH_2 groups of the silane interact with —COOH groups of the rubber, while $\text{—OC}_2\text{H}_5$ groups of the silane interact with —OH groups on the filler surface. Weak rubber-filler bonds formed during mixing are converted into a crosslinked structure during high-temperature molding. The extent of crosslinking of the rubber phase by the active sites on the filler surface is greater in the case of oxidized ISAF carbon black, as compared to the nonoxidized grade. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

The chemical reactivity of rubber-grade carbon black is attributed to the presence of oxygen-containing functional groups on its surface.¹⁻⁴ Chemical interaction between carbon black and rubber confers reinforcement to rubber in many instances.⁵⁻⁸ Polar rubbers are known to exhibit stronger interaction with carbon blacks as compared to the nonpolar rubbers.⁴ Recently, Roychowdhury and De^{9,10} reported that oxidized carbon black chemically reacts with epoxidized natural rubber and chlorosulfonated polyethylene, the extent of the reaction being dependent on the concentration of oxygen-containing functional groups on the carbon black surface. Plueddemann¹² showed that coupling agents can improve the rubber-filler interaction in the case of mineral fillers. Recently, Wang et al.¹³ showed that silane coupling agents increase the surface activity of carbon black filler and cause improvement in the rubber-filler interaction. In an earlier communication, it was reported that oxygen-containing groups

on the carbon black surface can act as a crosslinking agent for carboxylated nitrile rubber (XNBR).¹¹ Preliminary studies revealed that 3-aminopropyltriethoxysilane (APTS) enhances the degree of chemical interaction between XNBR and carbon black. The present article reports the results of the studies on the effect of APTS on the interaction between carbon black and XNBR. The carbon black studied included two grades, namely, ISAF carbon black and oxidized ISAF carbon black.

EXPERIMENTAL

Details of the materials used are given in Table I and the formulations of the mixes are shown in Table II. Mixing of carbon black, silane, and XNBR was done in a Brabender Plasticorder (PLE-330) at room temperature using a rotor speed of 60 rpm. The coupling agent, APTS, was added in drops 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 laboratory-size two-roll mill.

For bound rubber measurement, the mixes were conditioned at room temperature for 7 days and then

* To whom correspondence should be addressed.

Table I Details of Materials Used

Material	Characteristics	Source
Carboxylated nitrile rubber (XNBR) KRYNACK X 7.50	% acrylonitrile = 27 % carboxyl = 7 Mooney viscosity (M11 + 4 at 100°C), 50	Bayer Polysar, France
Oxidized ISAF black (Spezienschwarz-550)	DBP: 47 cc/100 g N ₂ SA: 110 m ² /g pH: 2.8, %0: 1.44	Degussa AG, Germany
ISAF black (Printex-55)	DBP: 45 cc/100 g N ₂ SA: 105 m ² /g pH: 9.5; %0: 0.9	Degussa AG, Germany
Coupling agent, 3-aminopropyltriethoxysilane	Specific gravity: 0.942 g/cc Boiling point: 217°C	Fluka Chemical Corp., USA

cut into small pieces. Approximately 0.5 g of each compound was immersed in 300 mL of chloroform for 24 h. The samples were taken out and then vacuum-dried to a constant weight. The bound rubber content was expressed as the weight percent of the unextracted and insolubilized rubber on the carbon black surface.

The cure characteristics of the compounds were studied in a Monsanto rheometer, MDR-2000, at a 0.5° arc of oscillation and at the curing temperature of 190°C. Molding of the samples was done at the same temperature under 10 MPa pressure in a hydraulic press for 60 min. The molded samples were taken out from the mold only after cooling them to room temperature under pressure by cold water circulation through the platens of the press.

Swelling of the molded samples was done in chloroform at room temperature for 72 h and then vacuum-dried to a constant weight. The results of the swelling experiments were expressed as the percentage weight loss of rubber on swelling. The physical properties were measured in a Zwick universal testing machine, Model 1445. Stress-strain properties of the molded samples were determined according to ASTM D-412 (1987), method A. Tear strength of the molded samples was measured using a 90° nick-cut crescent sample according to ASTM D-624 (1986). The tension set at 100% elongation was carried out with the tensile specimen. The samples were stretched for 10 min and then a relaxation time of 10 min was allowed according to ASTM D-412 (1987).

Table II Formulations of Different Mixes and the Corresponding Bound Rubber and the Results of Monsanto Rheometric Studies (i.e., M_L and ΔT Values)

Material	Mix Designation										
	X	XOB	XOB ₁	XOB ₂	XOB ₃	XOB ₄	XB	XB ₁	XB ₂	XB ₃	XB ₄
XNBR	100	100	100	100	100	100	100	100	100	100	100
Oxidized ISAF	—	75	75	75	75	75	—	—	—	—	—
ISAF	—	—	—	—	—	—	75	75	75	75	75
APTS	7.5	—	1.8	3.75	5.7	7.5	—	1.8	3.75	5.7	7.5
Bound rubber content (%)	—	19	21	24	29	35	15	17	19	21	24
M_L (dN-m)	1.0	10.5	7.3	6.0	5.7	4.9	10.9	8.1	6.9	5.6	5.0
ΔT (dN-m)	1.0	10.0	14.5	17.6	20.2	25.4	4.0	5.6	7.5	8.9	10.2

The dynamic mechanical properties were determined using a Rheovibron DDV-III-EP of Orientec Corp., Japan. The testing was performed at a frequency of 3.5 Hz and a double-strain amplitude (DSA) of 0.166%, and in the temperature range -100 to 200°C , the heating rate was $2^{\circ}\text{C min}^{-1}$. DSA is defined as $(2 \times A/L)$, where A is the amplitude of vibration, and L , the length of the sample. The low-strain dynamic properties were also determined using the same instrument, in the tension mode. The DSA was varied from 0.083 to 5%. The experiment was conducted at room temperature and at a frequency of 3.5 Hz.

RESULTS AND DISCUSSION

Figure 1 represents the Monsanto rheographs of the mixes. The M_L (the minimum torque) and Δt (the difference in torque rise between the measured torque at 60 min and the minimum torque) values are tabulated in Table II. If the mastication time is kept constant, the M_L value signifies the extent of filler-filler interaggregation¹⁴ and, therefore, the high value of M_L in the case of the XNBR-carbon black system is due to a high degree of filler-filler interaggregation. On the addition of APTS, the M_L value gradually decreases, indicating thereby a gradual reduction in the filler-filler interaggregation. It has been reported that use of the silane coupling agent was an effective means of reducing the viscosity.¹⁴⁻¹⁶ The reduction in viscosity is attributed to the structure breakdown of the filler-filler agglomerates. The results of the

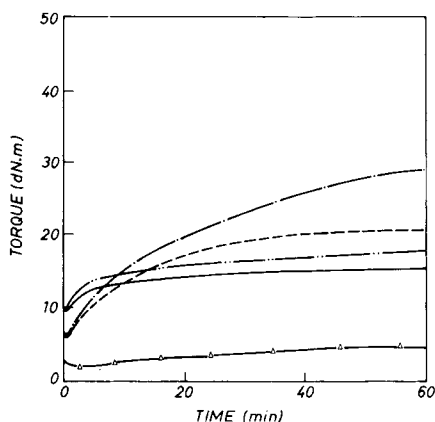


Figure 1 Monsanto Rheometric curves at 190°C : ($-\Delta-$) X; ($-\cdot-\cdot-$) XOB; ($—$) XB; ($-\cdot-\cdot-$) XOB₄; ($---$) XB₄.

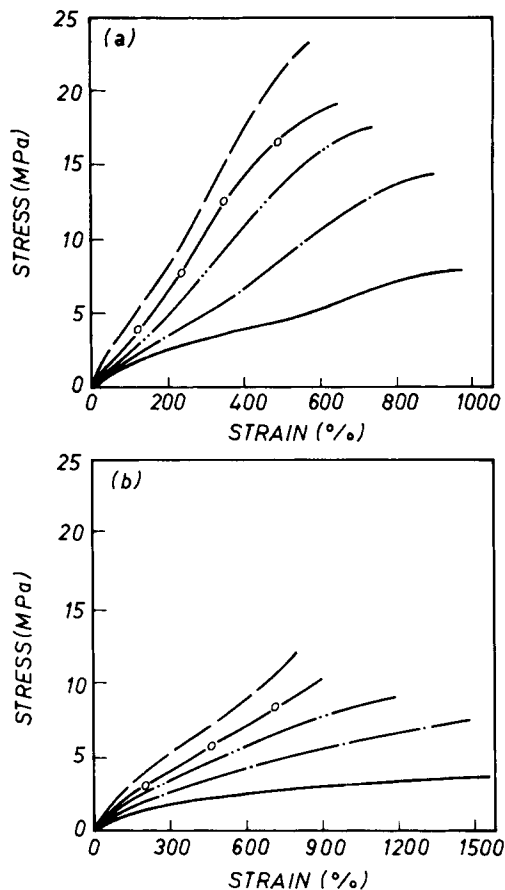


Figure 2 (a) Stress-strain plots of XNBR-oxidized ISAF carbon black systems molded at 190°C : ($—$) XOB; ($-\cdot-\cdot-$) XOB₁; ($-\cdot-\cdot-$) XOB₂; ($-\circ-$) XOB₃; ($---$) XOB₄. (b) Stress-strain plots of XNBR-ISAF carbon black systems molded at 190°C : ($—$) XB; ($-\cdot-\cdot-$) XB₁; ($-\cdot-\cdot-$) XB₂; ($-\circ-$) XB₃; ($---$) XB₄.

bound rubber measurements are summarized in Table II. Although the silane coupling agent improves the dispersion of the carbon black filler, the bound rubber increases and the effect is pronounced in the case of oxidized grade of carbon black as compared to the nonoxidized grade. As discussed later (Fig. 8), it is believed that the amino and ethoxy groups of the APTS interact with the carboxyl group of the XNBR and the oxygen-containing groups on the filler surface, respectively, thus increasing the bound rubber content.

The increase in Δt in the Monsanto rheograph is ascribed to the crosslinking of the rubber phase.¹¹ The Δt for the neat polymer is negligible, thus nullifying the possibility of thermovulcanization of the rubber. The Δt of XNBR-silane is also negligible,

which indicates the absence of crosslinking in the rubber phase in the presence APTS alone. Therefore, the rise in torque in the case of the XNBR-carbon black system is solely attributed to the reaction between the carboxylic groups of XNBR and the oxygen-containing groups on the filler surface.¹¹ The increase in Δt with increase in the concentration of the silane is evident from Figure 1. The results are summarized in Table II. Therefore, it can be inferred that APTS promotes the rubber-carbon black interface reaction. It is also further observed that the extent of the interfacial reaction is greater in the case of oxidized ISAF carbon black as compared to the nonoxidized grade.

The stress-strain properties of the molded samples are shown in Figure 2. The results of the measurements of the physical properties are summarized in Table III. The moduli at 100 and 300% elongation increase with increasing concentration of APTS. The tensile strength and the tear resistance also increase with the incorporation of the coupling agent, indicating enhanced rubber-filler interaction and this effect is more pronounced in the case of the oxidized grade as compared to the nonoxidized grade of carbon black. The drop in the tension set in the presence of APTS, particularly at high concentration, is indicative of the formation of a tight network. The solvent swelling results correlate directly with the Δt values of the rheometric study. The decrease

in the weight loss on swelling indicates a higher extent of the interfacial reaction in the presence of APTS.

Figures 3 and 4 show the results of the dynamic mechanical analyses of the XNBR-carbon black system in the presence of APTS. At T_g , the $\tan \delta_{\max}$ decreases while the storage modulus (E') at room temperature increases, as the APTS concentration increases. The effect is more pronounced in the case of the oxidized ISAF black, as compared to the ISAF black. As the modulus of a crosslinked polymer is proportional to the crosslinked density, according to the statistical theory of rubber elasticity,¹⁷ the enhancement in the modulus in the present case is thus attributed to the increased interfacial reaction in the presence of APTS, particularly in the case of oxidized ISAF carbon black. This is also responsible for the depression of $\tan \delta_{\max}$ at T_g . The dependence of the storage modulus at 25°C and the loss tangent at T_g (i.e., $\tan \delta_{\max}$) on the loading of APTS is shown in Figure 5 and they are found to obey the following equations:

(a) For oxidized ISAF carbon black,

$$E'_{(c)}/E' = 1 + 2.0 C - 0.25 C^2 \quad (1)$$

$$\begin{aligned} (\tan \delta_{\max})_c / \tan \delta_{\max} \\ = 1 - 0.1 C + 0.01 C^2 \quad (2) \end{aligned}$$

Table III Physical Properties at 25°C of the XNBR-oxidized ISAF Black Mixes Molded at 190°C^a

Properties	Mix Designation				
	XOB	XOB ₁	XOB ₂	XOB ₃	XOB ₄
100% modulus (MPa)	2.9 (1.4)	2.8 (1.9)	3.2 (2.0)	4.2 (2.1)	4.3 (2.7)
300% modulus (MPa)	3.7 (1.7)	4.9 (2.6)	7.0 (3.5)	8.3 (5.1)	12.3 (6.3)
Tensile strength (MPa)	8.1 (3.4)	14.2 (6.1)	16.8 (7.8)	19.2 (10.4)	24.1 (11.9)
Elongation at break (%)	988 (1682)	902 (1402)	790 (1105)	654 (833)	582 (702)
Tear strength (N/mm)	32.0 (21.9)	48.7 (32.4)	58.9 (40.2)	77.1 (49.6)	90.9 (55.6)
Tension set (%)	15.0 (20.0)	7.5 (10.0)	5.0 (7.5)	5.0 (5.0)	0 (2.5)
% Weight loss on swelling	49 (61)	28 (36)	18 (31)	11 (25)	6 (18)

^a Values in parentheses are the results of the mixes with the corresponding nonoxidized carbon black (i.e., mix nos. XB₁, XB₂, XB₃, and XB₄).

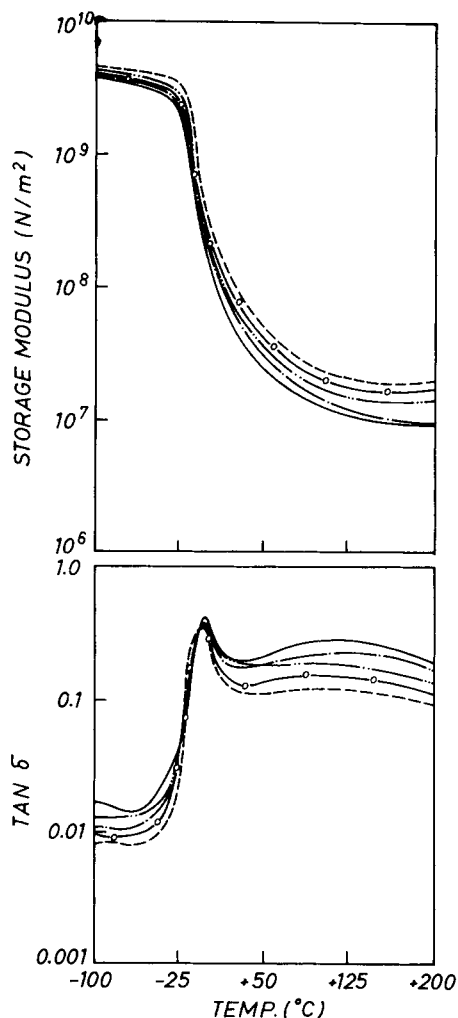


Figure 3 Storage modulus and loss tangent vs. temperature plots of XNBR-oxidized ISAF carbon black systems molded at 190°C: (—) XOB; (-·-) XOB₁; (-· ·-) XOB₂; (-○-) XOB₃; (- - -) XOB₄.

(b) For ISAF carbon black,

$$E'_{(c)}/E' = 1 + 1.4 C - 0.17 C^2 \quad (3)$$

$$\begin{aligned} (\tan \delta_{\max})_c / \tan \delta_{\max} \\ = 1 - 0.07 C + 0.008 C^2 \quad (4) \end{aligned}$$

where C is the loading of APTS in parts per hundred parts of rubber by weight, $E'_{(c)}$ and $(\tan \delta_{\max})_c$ refer to APTS-containing formulations, and E' and $\tan \delta_{\max}$ refer to mixes without APTS.

The variation of the in-phase storage modulus with % DSA for the XNBR-carbon black system at different loadings of APTS is shown in Figure 6.

The results of the measurements of low-strain dynamic mechanical properties are summarized in Table IV. Expectedly, the storage modulus decreases with increase in % DSA. The difference $\Delta E'$ [i.e., $(E'_0 - E'_\infty)$, where E'_0 is the storage modulus at low strain (0.083%) and E'_∞ is the storage modulus at high strain (5%)] is believed to be due to structure breakdown of the filler-filler networks.^{18,19} Since $\Delta E'$ is the highest in the absence of APTS and it decreases with increasing concentration of the APTS, it is inferred that the low-strain storage modulus, which is mainly due to the filler-filler networking, decreases on formation of the rubber-filler network. On application of a dynamic strain, the filler-filler

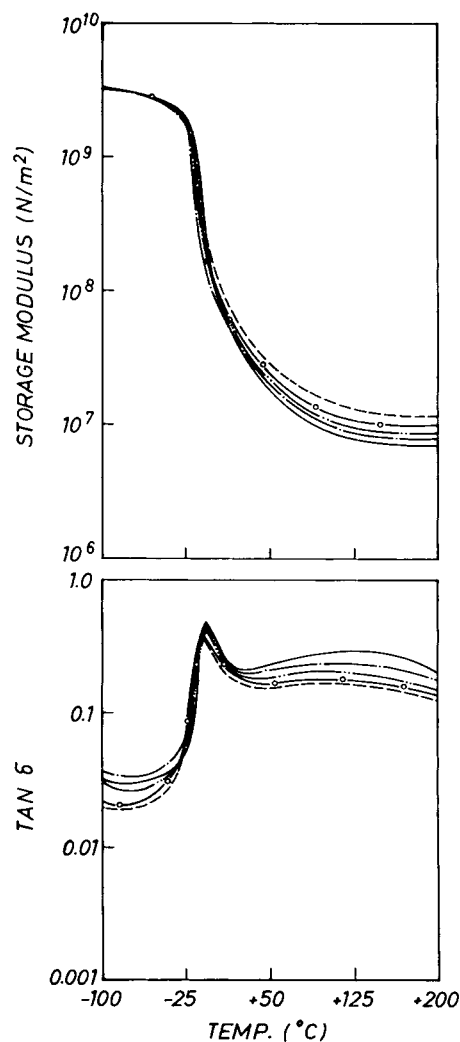


Figure 4 Storage modulus and loss tangent vs. temperature plots of XNBR-ISAF carbon black systems molded at 190°C: (—) XB; (-·-) XB₁; (-· ·-) XB₂; (-○-) XB₃; (- - -) XB₄.

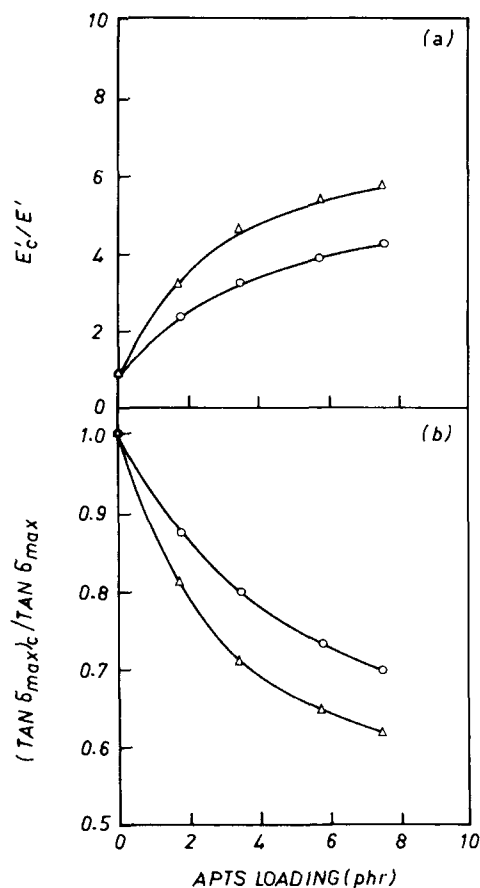


Figure 5 (a) Variation of storage modulus at 25°C with loading of APTS: (—△—) XNBR-oxidized ISAF carbon black; (—○—) XNBR-ISAF carbon black. (b) Variation of $\tan \delta_{max}$ at T_g with loading of APTS: (—△—) XNBR-oxidized ISAF carbon black; (—○—) XNBR-ISAF carbon black.

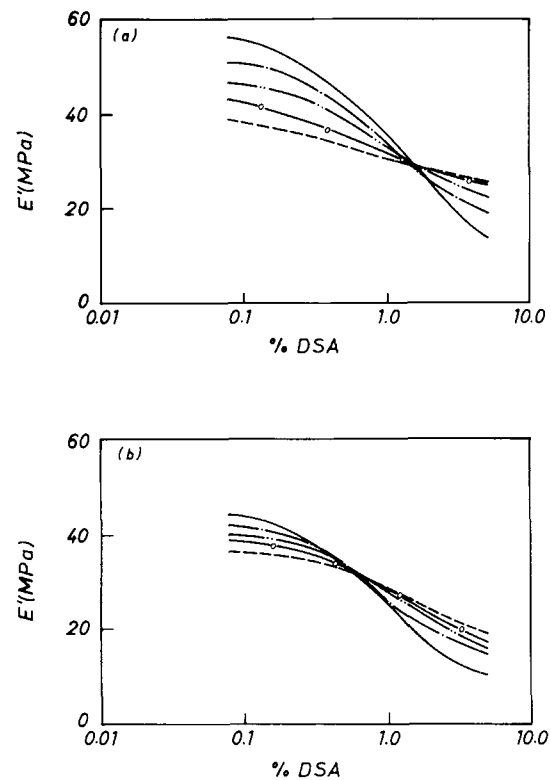


Figure 6 (a) Plots of storage modulus vs. % DSA of XNBR-oxidized ISAF carbon black systems molded at 190°C: (—) XOB; (—·—) XOB₁; (—··—) XOB₂; (—○—) XOB₃; (---) XOB₄. (b) Plots of storage modulus vs. % DSA of XNBR-ISAF carbon black systems molded at 190°C: (—) XB; (—·—) XB₁; (—··—) XB₂; (—○—) XB₃; (---) XB₄.

Table IV The Low-strain Dynamic Properties at 25°C of the Different XNBR-Black Mixes Molded at 190°C

Mix Designation	Storage Modulus at 0.083% DSA, E'_0 (MPa)	Storage Modulus at 5% DSA, E'_α (MPa)	$\Delta E'$, ($E'_0 - E'_\alpha$) (MPa)
XOB	57.7	12.1	45.6
XOB ₁	52.3	18.0	34.3
XOB ₂	44.9	20.2	24.7
XOB ₃	41.1	23.3	17.8
XOB ₄	38.2	25.5	12.7
XB	42.6	9.3	33.3
XB ₁	41.0	15.4	25.6
XB ₂	40.1	16.3	23.8
XB ₃	38.4	17.6	20.8
XB ₄	37.6	18.5	19.1

networks readily undergo breakdown, but a similar breakdown does not occur in the case of the rubber–filler bonds and, hence, $\Delta E'$ decreases. Due to stronger interaction between the rubber and the oxidized black, the decrease in $\Delta E'$ in the presence of APTS is pronounced in the case of oxidized ISAF carbon black, as compared to the nonoxidized grade.

Ayala et al.²⁰ proposed a rubber–filler interaction parameter (I), which is defined as

$$I = \sigma / \eta \quad (5)$$

where σ is the slope of the stress–strain curve in the relatively linear region and η is the filler–filler networking parameter, calculated from the ratio of storage modulus values at high strain and low strain. Figure 7 shows that the rubber–filler interaction parameter (I) increases with increase in the loading of APTS, while the filler–filler networking factor (η) gradually decreases. The increase in I and the

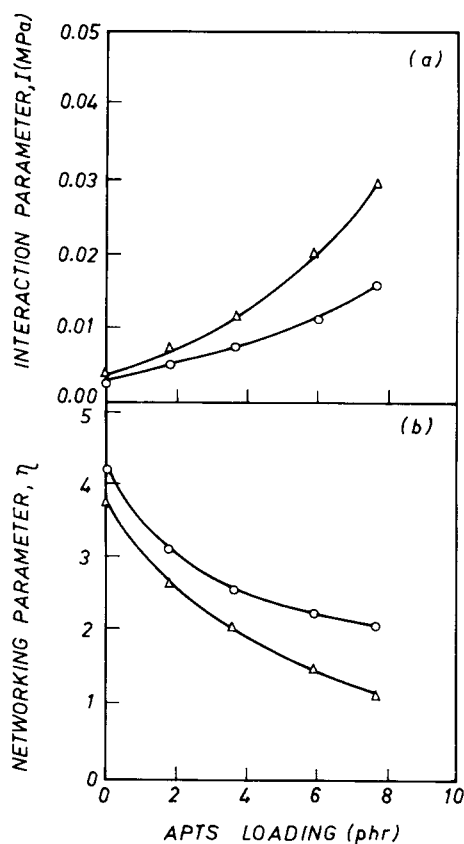


Figure 7 (a) Variation of interaction parameter (I) with loading of APTS: (— Δ —) XNBR–oxidized ISAF carbon black; (— \circ —) XNBR–ISAF carbon black. (b) Variation of networking parameter (η) with loading of APTS: (— Δ —) XNBR–oxidized ISAF carbon black; (— \circ —) XNBR–ISAF carbon black.

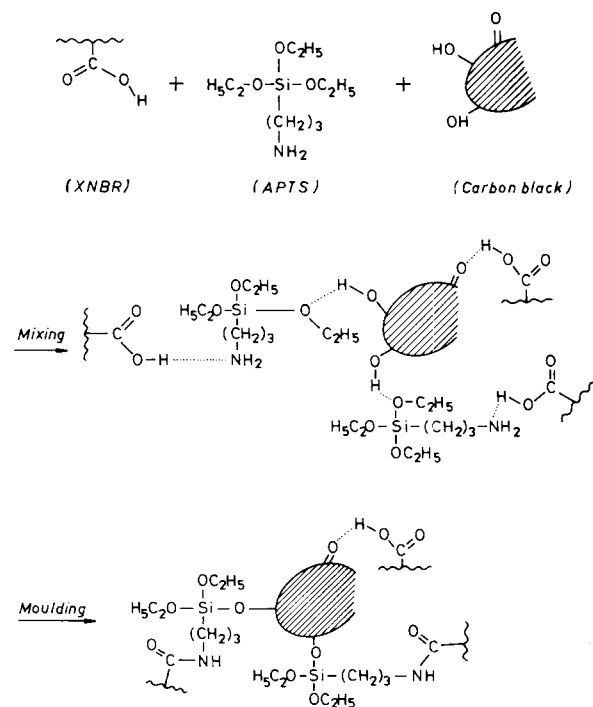


Figure 8 Schematic representation of the probable mechanism occurring in the XNBR–carbon black system.

decrease in η is more prominent in the case of oxidized ISAF carbon black, as compared to the non-oxidized grade. It is concluded that in the XNBR–carbon black system, APTS plays a dual role. On the one hand, it reduces the filler–filler interaction and thus improves the dispersion of the carbon black, and, on the other hand, it assists in the cross-linking of the rubber phase by the filler.

It has been proposed earlier that the —OH group on the carbon black surface interacts chemically with the —COOH groups of XNBR.¹¹ It is believed that APTS participates in the interaction mechanism through its amino and ethoxy groups. Figure 8 shows a probable mechanism of the XNBR–carbon black bonding in the presence of APTS. On the basis of the results of infrared spectroscopic studies, formation of —CONH— groups has been reported in the bonding between XNBR and —OH groups of precipitated silica filler in the presence of APTS.²¹

CONCLUSIONS

High-temperature molding of XNBR–carbon black mixes causes crosslinking of the rubber phase by the chemically reactive sites on the filler surface. Monsanto rheometric studies of the rubber–filler mixes and measurements of the physical and dynamic me-

chanical properties of the molded samples reveal that incorporation of aminopropyltriethoxysilane to the XNBR-carbon black system causes a manyfold increase in the rubber-filler bonding at the expense of the filler-filler networks.

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REFERENCES

1. M. L. Studebaker, *Rubb. Chem. Technol.*, **30**, 1400 (1957).
2. R. C. Bansal, J. B. Donnet, and F. Stoeckli, *Active Carbon*, Marcel Dekker, New York, 1988.
3. J. B. Donnet and A. Vidal, *Adv. Polym. Sci.*, **76**, 103 (1986).
4. M. J. Wang, S. Wolff, and J. B. Donnet, *Rubb. Chem. Technol.*, **64**, 714 (1991).
5. G. Kraus, in *Science and Technology of Rubbers*, F. R. Eirich, Ed., Academic Press, New York, 1965, Chap. 8, p. 339.
6. G. Kraus, *Angew. Makromol. Chem.*, **60/61**, 215 (1971).
7. A. M. Gessler, *Rubb. Age*, **74**, 423 (1953).
8. A. Asai, H. Kaneki, M. Sumita, and K. Myasaka, *J. Appl. Polym. Sci.*, **43**, 1253 (1991).
9. A. Roychowdhury and P. P. De, *J. Appl. Polym. Sci.*, **50**, 181 (1993).
10. A. Roychowdhury, S. K. De, P. P. De, J. A. Ayala, and G. A. Joyce, *Rubb. Chem. Technol.*, **67**, 667 (1994).
11. S. Bandyopadhyay, P. P. De, D. K. Tripathy, and S. K. De, *J. Appl. Polym. Sci.*, **58**, 719 (1995).
12. E. P. Plueddemann, *Silane Coupling Agents*, Plenum Press, New York, 1982.
13. W. D. Wang, A. Vidal, G. Nause, and J. B. Donnet, *Kautsch. Gummi Kunstst.*, **47**, 493 (1994).
14. S. K. Mondal and D. K. Basu, *Rubb. Chem. Technol.*, **67**, 672 (1994).
15. S. Wolff, K. Burmester, and E. H. Tan, Paper presented at the *International Conference of DKG*, Munich, Sept. 2-5, 1974.
16. P. P. G. Industries, Inc., Hi-sil Bulletin No. 41, Jan. 1971.
17. L. R. G. Treolar, *The Physics of Rubber Elasticity*, 3rd ed., Clarendon Press, Oxford, 1975.
18. A. R. Payne, *J. Appl. Polym. Sci.*, **6**, 57 (1962).
19. A. R. Payne and R. E. Whittaker, *Rubb. Chem. Technol.*, **44**, 440 (1971).
20. J. A. Ayala, W. M. Hess, G. A. Joyce, and F. D. Kistler, *Rubb. Chem. Technol.*, **66**, 772 (1993).
21. S. Bandyopadhyay, P. P. De, D. K. Tripathy, and S. K. De, *Rubb. Chem. Technol.*, to appear.

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