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Influence of surface oxidation of carbon black on its interaction with nitrile rubbers

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Interactions of carbon black with nitrile rubber (NBR) and carboxylated nitrile rubber (XNBR) were studied by measurements of bound rubber, physical and dynamic mechanical properties of the vulcanizates and Monsanto rheometric studies on the rubber–filler mixes. Compared with NBR, XNBR shows a higher degree of interaction with the filler and oxidation of the filler surface increases the extent of the rubber–filler bonding, which involves weak hydrogen bonding and Van der Waal's forces. In the case of XNBR additional chemical bonding occurs between the –COOH groups of the rubber and the reactive groups on the filler surface.

(Keywords: oxidation; carbon black; nitrile rubber)

Introduction

The morphology of carbon black, and in particular that of its surface area, plays an important role in the reinforcement of rubber[1,2], which is believed to be caused by Van der Waal's type interaction between rubber and filler[3]. Chemical interaction between rubber and the carbon black surface is believed to contribute towards the reinforcement of rubber in many instances[4–6]. Surface-oxidized carbon black has been reported to enhance the reinforcement of butyl rubber[5] and natural rubber[6]. Chemical reactivity of the rubber-grade furnace blacks is attributed to the presence of oxygen-containing functional groups such as phenol, quinone, carboxyl and lactone[7–10].

While there exists evidence of chemical interactions between carbon black surfaces and functionalized polymers[11,12], the role of carbon black surface chemistry in the mechanism of the reinforcement of rubber is not clearly understood. The present paper reports the results of studies on the effect of rubber–filler interaction on the physical and dynamic mechanical properties of nitrile rubbers. The extent of rubber–filler interaction was varied by using two types of rubber, that is, nitrile rubber (NBR) and carboxylated nitrile rubber (XNBR), and two grades of intermediate superabrasion furnace carbon black (ISAF black) of different surface oxygen contents.

Experimental

Details of the materials used are given in *Table 1* and the formulations of the different mixes are given in *Tables 2* and *3*. Mixing of the carbon black with the rubber was done in a Brabender Plasticorder (model PLE-330), fitted with a cam-type rotor, for 8 min at room temperature; the rotor speed was 60 rev min^{-1}. The rubber–filler mix was taken out and sheeted in a cold laboratory-sized two-roll mixing mill. In mixes containing curing agents and other additives, the ingredients were added on the mixing mill.

For the determinations of bound rubber, the rubber–carbon black mixes were conditioned at room temperature and then cut into small pieces, which were kept immersed in chloroform at room temperature for 24 h. The samples were then taken out and vacuum dried to constant weight. The bound rubber content in the given mix was expressed as the percentage of insolubilized rubber in the total rubber.

The rheometric studies of the mixes were done at 190°C in a Monsanto R-100 rheometer with an arc of oscillation of 3°. The samples containing curing agents (*Table 2*) were moulded at 190°C for the optimum cure times. The mixes without curvatives (*Table 3*) were moulded at the same temperature for 60 min. Moulding was done at 10 MPa pressure in a laboratory-sized hydraulic press.

Swelling of the moulded samples was done in chloroform at room temperature for 72 h to achieve

Table 1 Details of materials used

Material	Characteristics	Source
Carboxylated acrylonitrile rubber (XNBR) KRYNACK × 7.50	wt% acrylonitrile = 27 wt% carboxyl = 7 Mooney viscosity (ML_{1+4} at 100°C), 50	Bayer Polysar, France
Acrylonitrile–butadiene rubber (NBR) KRYNACK 34.50	wt% acrylonitrile = 34 Mooney viscosity (ML_{1+4} at 100°C), 50	Bayer Polysar, France
Oxidized ISAF black (Spezialschwarz-550)	DBP[a]: 47 ml/100 mg N_2SA[b]: 110 m^2/g pH 2.8, %0: 1.44	Degussa AG, Germany
ISAF black (Printex-55)	DBP: 45 ml/100 mg N_2SA: 105 m^2/g pH 9.5, %0: 0.9	Degussa AG, Germany

[a] Di-butyl phthalate
[b] Nitrogen surface area

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equilibrium swelling and then dried to constant weight. The results are expressed as percentage weight loss of the sample. The stress–strain properties were measured according to ASTM D-412-87 in a Zwick Universal Testing Machine (model 1445). The abrasion resistance of the samples was measured according to BS 903: Part A: 1957–Method C, in a Dupont Abrasion

Table 2 Formulations containing curing agents and the corresponding optimum cure times at 190° C

Material	Mix designation X	XB	XOB	N	NB	NOB
XNBR	100	100	100	—	—	—
NBR	—	—	—	100	100	100
Zinc oxide	2.5	2.5	2.5	2.5	2.5	2.5
Stearic acid	1.5	1.5	1.5	1.5	1.5	1.5
ISAF black	—	75	—	—	75	—
Oxidized ISAF black	—	—	75	—	—	75
Sulfur	0.3	0.3	0.3	0.3	0.3	0.3
MBTS[a]	1.0	1.0	1.0	1.0	1.0	1.0
TMT[b]	—	—	—	0.5	0.5	0.5
Optimum cure time at 190° C (min)	5	7	11	7	10	13

[a] Mercaptodibenzthiazolyl disulfide
[b] Tetramethyl thiuram disulfide

Table 3 Formulations of the rubber–filler mixes not containing any curative and the corresponding Δt[a] values and bound rubber content

Materials	Mix number 1	2	3	4
XNBR	100	100	—	—
NBR	—	—	100	100
ISAF black	—	75	—	75
Oxidized ISAF black	75	—	75	—
Δt values (dN m)	16	10	6	4
Bound rubber content (%)	19	16	17	15

[a] The difference between the torque at 60 min and the minimum torque

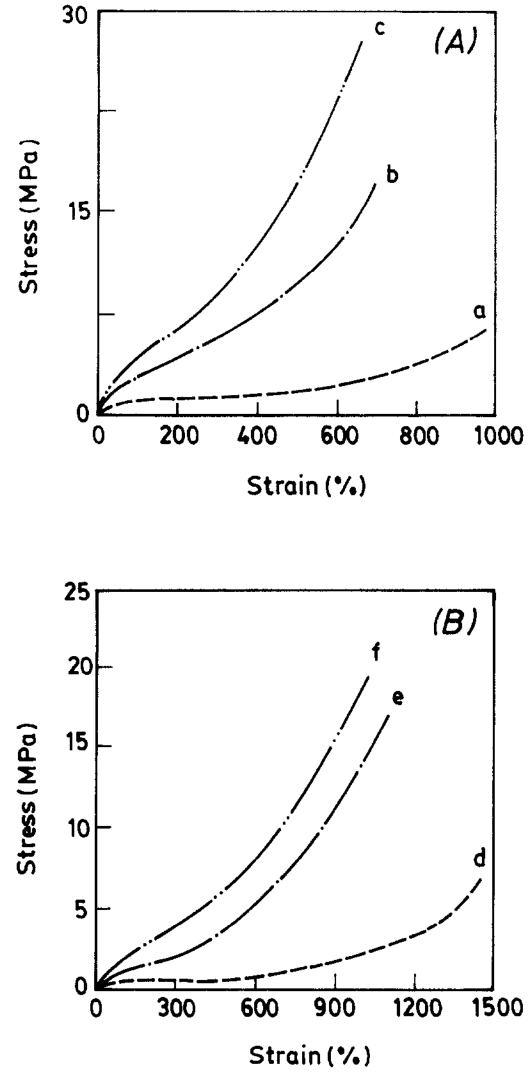

Figure 1 (A) Stress–strain properties for the XNBR vulcanizates moulded at 190° C for optimum cure time: (a) unfilled; (b) ISAF black; (c) oxidized ISAF black. (B) Stress–strain properties for the NBR vulcanizates moulded at 190°C for optimum cure time: (d) unfilled; (e) ISAF black; (f) oxidized ISAF black

Table 4 Physical properties of the vulcanizates at 25°C[a,b]

Properties	Mix designation X	XB	XOB	N	NB	NOB
100% modulus (MPa)	1.0	3.9 (1.3)	4.3 (2.9)	0.5	1.6 (1.1)	1.4 (1.7)
300% modulus (MPa)	1.5	10.9 (1.6)	12.5 (3.7)	0.7	2.9 (1.5)	3.6 (2.3)
Tensile strength (MPa)	7.6	18.4 (3.3)	27.8 (8.1)	6.4	17.6 (2.4)	20.8 (5.2)
Elongation at break (%)	988	597 (1682)	509 (988)	1400	1018 (1807)	800 (1512)
Tear strength (kN mm^{-1})	0.018	1.85 (0.022)	2.2 (0.032)	0.016	0.085 (0.018)	0.098 (0.023)
Hardness (Shore A)	46	70	82	36	52	60
Hysteresis loss (J m^{-2}) × 10^3	15	93	115	5	30	33
Abrasion loss (cm^3 h^{-1})	0.34	0.04	0.02	0.5	0.05	0.04
% weight loss in swelling in chloroform	13	8 (61)	4 (49)	15	11 (80)	9 (68)

[a] Figures in parentheses indicate the results of the rubber–filler mixes, not containing any curative
[b] 300% modulus (MPa), 70°C: X, 0.8; XB, 3.1; XOB, 4.7; N, 0.6; NB, 1.9; NOB, 2.0

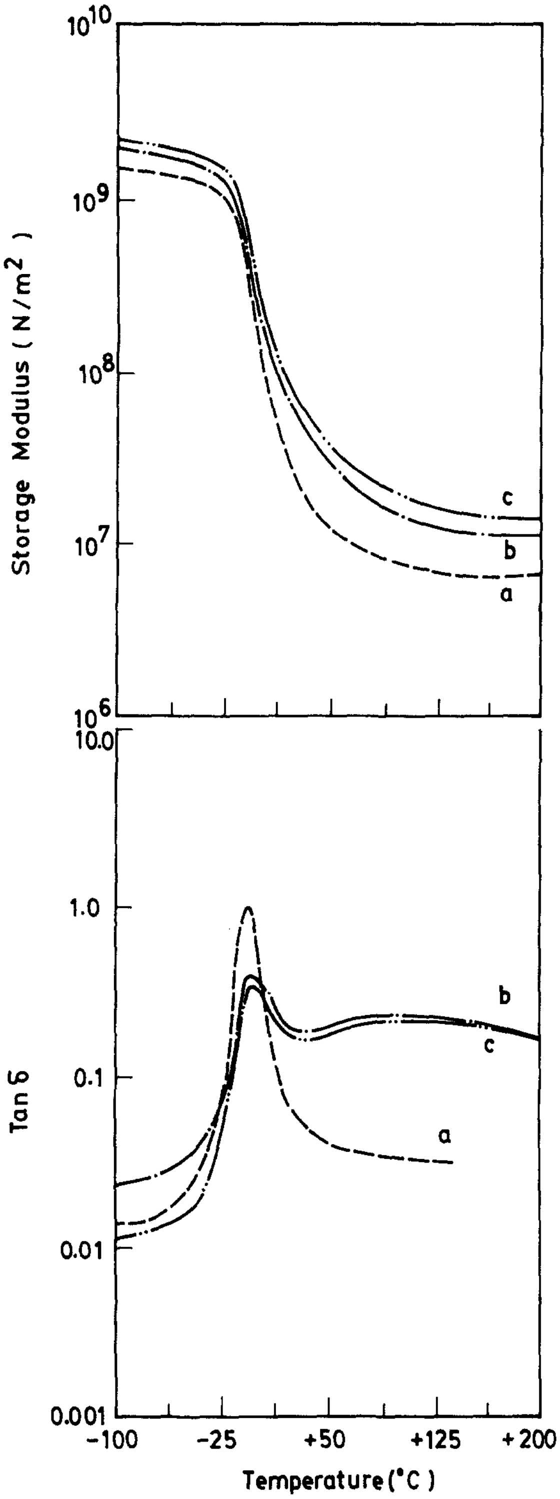

Figure 2 Storage modulus and tan δ plots for the XNBR vulcanizates moulded at 190°C for optimum cure time: (a) unfilled; (b) ISAF black; (c) oxidized ISAF black

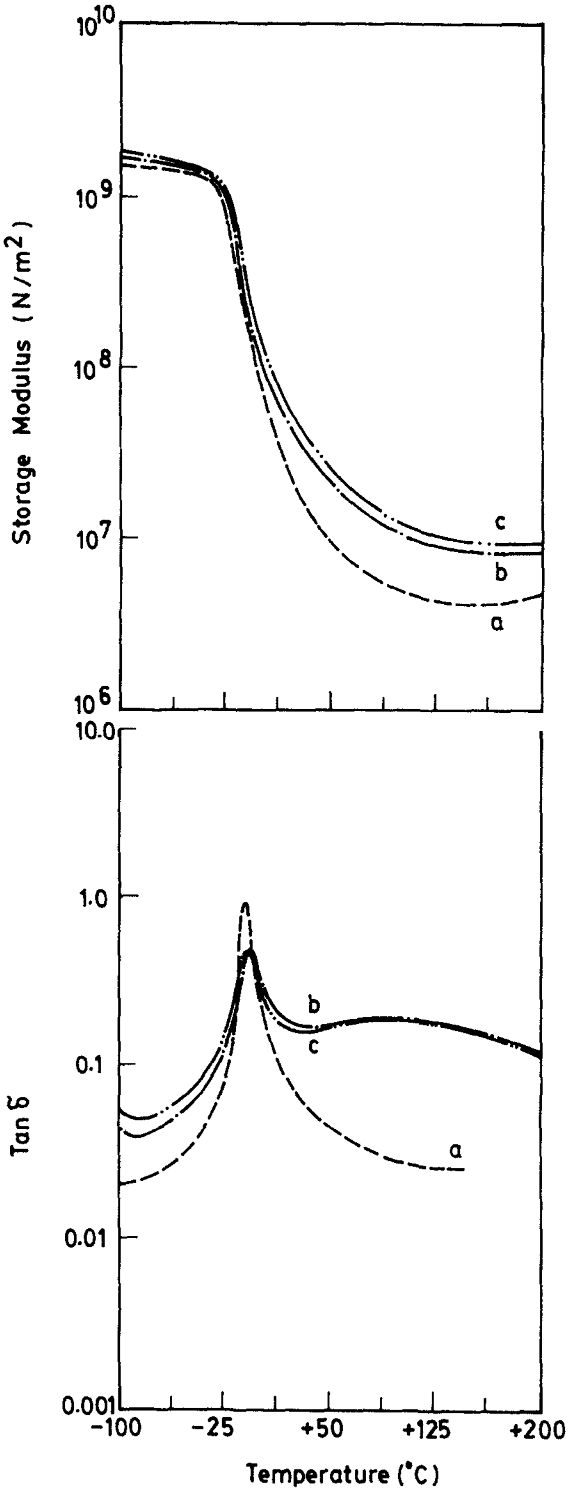

Figure 3 Storage modulus and tan δ plots for the NBR vulcanizates moulded at 190°C for optimum cure time: (a) unfilled; (b) ISAF black; (c) oxidized ISAF black

Tester. The hysteresis measurements were carried out with a dumbbell-shaped test specimen according to ASTM D-412-80 in a Zwick Universal Testing Machine (model 1445) at 100% elongation. The dynamic mechanical properties were studied using a Rheovibron (model DDV-III-EP, Orientec Corp., Japan) at a frequency of 3.5 Hz and a double strain amplitude of 0.166% in tension mode. The temperature scan was made from -100 to $+200$°C with an equilibrium linear rise of 2°C min^{-1}.

Table 5 Tan δ at T_g (−9°C) and storage modulus at 25°C of the vulcanizates

	Mix designation					
	X	XB	XOB	N	NB	NOB
Tan δ	1.02	0.36	0.33	1.15	0.47	0.47
Storage modulus ($\times 10^{-8}$) ($\mathrm{N\,m^{-2}}$)	0.49	6.9	9.8	0.32	5.0	6.5

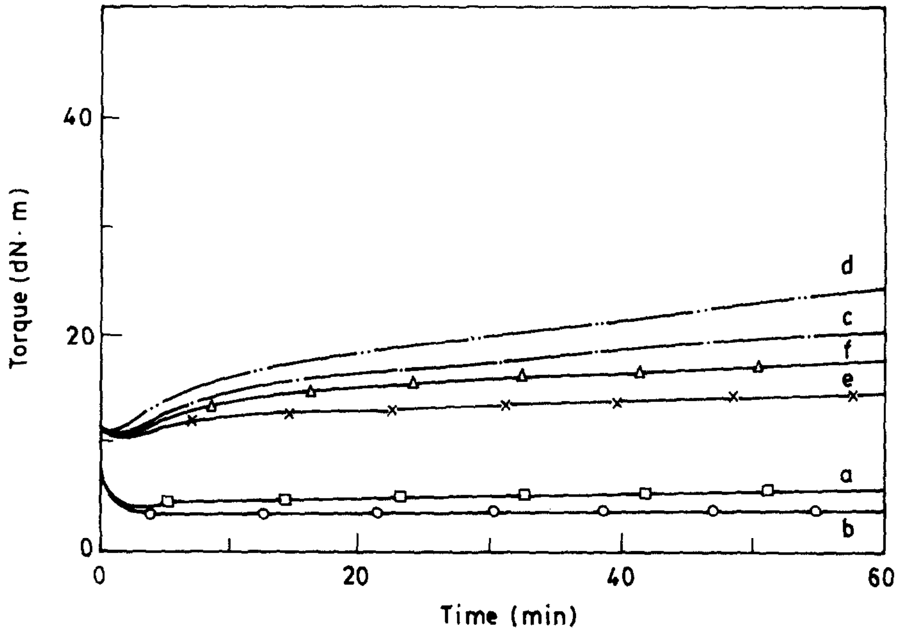

Figure 4 Monsanto rheographs of the rubber–filler mixes not containing any curatives (*Table 3*) at 190°C: (a) XNBR (unfilled); (b) NBR (unfilled); (c) XNBR–ISAF black; (d) XNBR–oxidized ISAF black; (e) NBR–ISAF black; (f) NBR–oxidized ISAF black

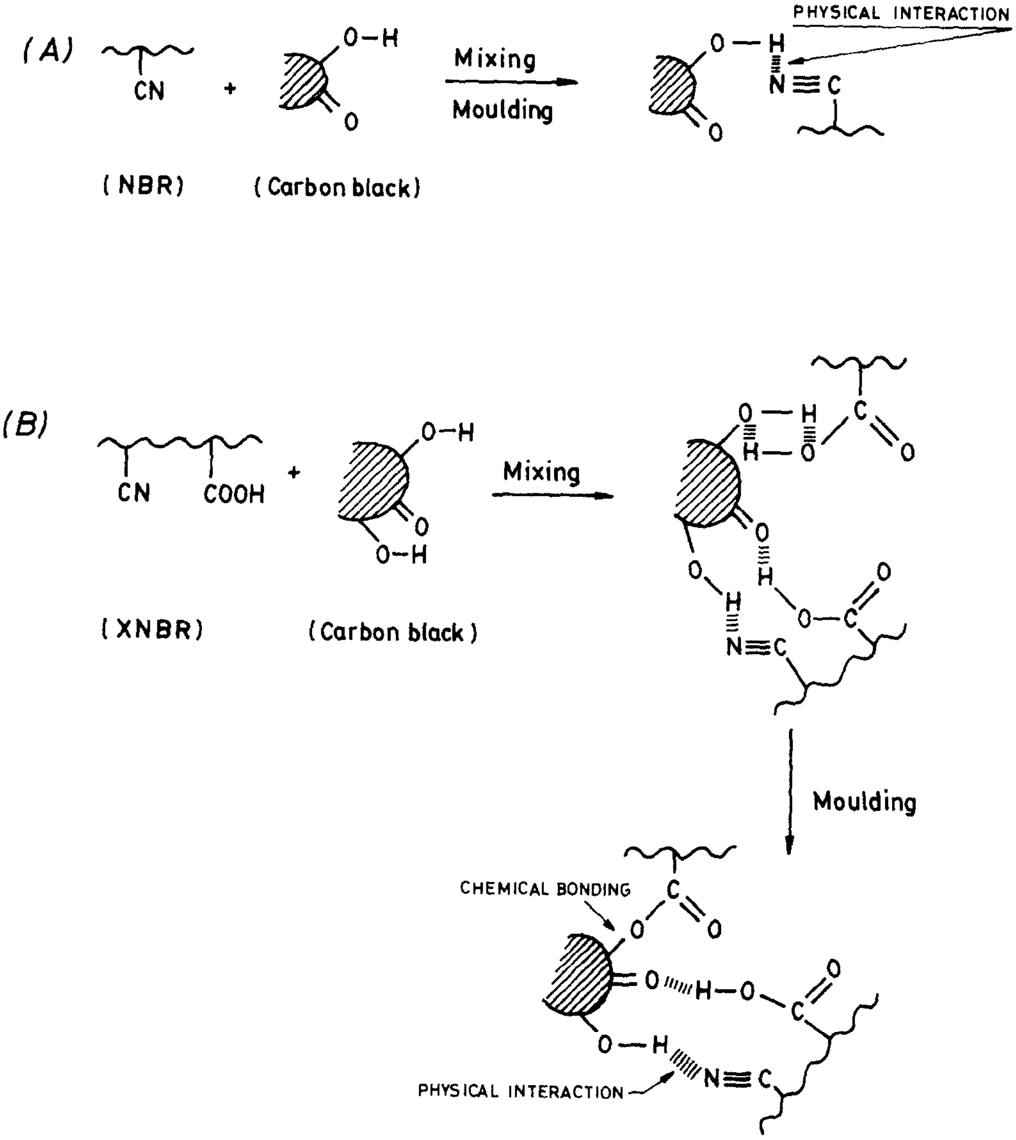

Figure 5 Probable mechanism of bonding in (A) NBR–carbon black and (B) XNBR–carbon black systems

Results and discussion

The results of measurement of physical properties are summarized in *Table 4*. *Figure 1* shows the effect of carbon black on the stress–strain properties of XNBR and NBR vulcanizates. It is observed that both modulus and tensile strength increase with the incorporation of filler, but the increase is more pronounced in the case of oxidized ISAF carbon black in both XNBR and NBR. Furthermore, the strength properties of XNBR vulcanizates are higher as compared to those of NBR vulcanizates. In both XNBR and NBR vulcanizates oxidation of carbon black causes an increase in hysteresis loss and the loss is higher in the case of XNBR compared with NBR. Results of solvent swelling studies reveal that the percentage of weight loss on swelling in chloroform decreases on incorporation of filler, and the decrease is more pronounced in the oxidized grade of carbon black in both XNBR and NBR. It is also observed that the percentage weight loss on swelling is less in the case of XNBR vulcanizates compared with NBR vulcanizates. When the 300% modulus (that is, the stress value at 300% elongation) of NBR vulcanizates was measured at 70°C, both grades of ISAF carbon black showed similar values, but in the case of XNBR vulcanizates the oxidized grade of ISAF carbon black registered a higher modulus (*Table 4*). It is, therefore, apparent that both XNBR and NBR interact with ISAF carbon black filler and the surface oxidation of the filler causes an increase in the extent of bonding, which is more pronounced in the case of XNBR. Interaction between NBR and the carbon black surface is believed to be due to hydrogen bonding and Van der Waal's forces and the extent of interaction increases as the oxygen content on the filler surface increases. This is evident from the results of bound rubber measurements. The presence of –COOH groups in XNBR causes an increase in the extent of bound-rubber formation, compared with the NBR–carbon black mixes. Here, also, the oxidized black shows higher bound-rubber content compared with the non-oxidized black. During moulding, additional interaction between the rubber and the filler is likely to occur, particularly in the case of XNBR vulcanizates, due to chemical bonding between the –COOH groups of the rubber and the reactive groups on the filler surface. The concentration of these reactive groups is increased by surface oxidation.

Figures 2 and *3* show the effects of the two types of carbon black on the storage moduli and the loss tangents of XNBR and NBR vulcanizates. It is seen that incorporation of carbon black causes changes in the dynamic mechanical properties of the rubbers, as is normally observed in the case of filled rubber vulcanizates[13–15]. The results are summarized in *Table 5*. It is seen that with increase in the extent of surface oxidation, $\tan\delta$ at T_g decreases and the storage modulus at room temperature increases; both indicate strong rubber–filler bonding[13–15]. The changes are larger in the case of XNBR systems.

Figure 4 shows Monsanto rheographs of the rubber–filler mixes containing no curatives (*Table 3*). There is no increase in the rheometric torque with time at 190°C in the case of unfilled polymers, showing that thermovulcanization does not occur. In the presence of carbon black, the NBR systems show only marginal increases in torque, while the XNBR system registers significant torque increases, particularly in the case of oxidized ISAF carbon black filler. The physical properties of the moulded rubber–filler mixes (*Table 4*) are moderate, indicating the occurrence of chemical bonding between the rubber and the filler surface, particularly when the rubber is XNBR and the filler is oxidized ISAF carbon black. A schematic representation of the interactions between the nitrile rubbers and carbon black is shown in *Figure 5*. Similar types of rubber–filler bonding have been reported earlier in the case of epoxidized natural rubber[11] and chlorosulfonated polyethylene[12].

Conclusion

Physical and dynamic mechanical properties and Monsanto rheometric studies reveal that the –COOH groups of XNBR interact chemically with the reactive groups of the ISAF black. Oxidation of the filler surface causes an increase in the extent of the rubber–filler bonding.

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