# Elastomer–Carbon Black Interaction: Influence of Elastomer Chemical Structure and Carbon Black Surface Chemistry on Bound Rubber Formation

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## SYNOPSIS

The contribution of elastomer polarity and reactivity to bound rubber formation has been investigated. In this study, a number of elastomers of different chemical nature have been tested. The surface of the carbon black (N110) has also been modified by nitric acid oxidation in order to increase the concentration of surface functional groups. The experimental results have shown that the bound rubber formation is barely related to the polarity of the polymers. It is the reactive sites in both the elastomer and carbon black which are mainly responsible for bound rubber formation. It therefore appears that the elastomer/carbon black interaction leading to the formation of bound rubber is essentially a chemical process involving primary bond formation between elastomer and carbon black. The oxidized carbon black exhibits a higher surface activity which may be due to an increased concentration of oxygen-containing reactive surface sites, namely, phenolic hydroxyl, carboxyl, lactone, and quinone groups. © 1995 John Wiley & Sons, Inc.

## INTRODUCTION

The reinforcement of an elastomer by a filler is associated with a strong interaction between the filler surface and elastomer.[1] Although a complete knowledge of the exact nature of elastomer/filler interaction is still lacking, the polymer/filler attachments appear to be both physical and chemical, depending on the physicochemical character of the filler surface and the chemical nature of the elastomer.[2] It is common knowledge that the morphology of carbon black, and in particular, its particle size, is much more important for elastomer reinforcement than the chemical energy available at the surface of the filler.[3] However, the morphology of carbon black is not sufficient to impart high reinforcement levels in saturated or nearly saturated rubbers, for instance, ethylene-propylene rubber (EPR) and butyl rubber (IIR). Gessler[4] showed that oxidized carbon blacks, as compared to untreated blacks, imparted much better reinforcement to butyl rubber, especially

when heated to high temperatures. He attributed this behavior to the reactions of oxygenated surface groups of carbon black with double bonds of the elastomer.[5] Surprisingly, even with highly unsaturated elastomers, such as, natural rubber and SBR, oxidized carbon blacks also lead to the formation of a higher amount of bound rubber.[6,7] According to Serizawa et al.,[6] this is due to an attenuation of interactions between carbon black and elastomer. Asai et al.,[7] however, have a different opinion; they asserted that the increase of bound rubber in these particular systems was a consequence of enhanced carbon black/elastomer interaction. Anyway, whatever the interpretation would be, this increase in bound rubber with increasing surface functionality of carbon blacks probably illustrates that bound rubber formation of carbon blacks and elastomers, at least with natural rubber and SBR, is not entirely a physical process.

In previous studies,[8,9] we observed that the polar rubbers (both saturated and unsaturated), having reactive functional groups (e.g., chlorosulfonated polyethylene and epoxidized natural rubber) showed much higher affinity for oxidized carbon blacks. On the other hand, polyethylacrylate, a saturated polar

rubber but without any reactive functional group exhibits a much weaker interaction with carbon blacks.[10] However, the nature of the interaction, in particular the importance of the carbon black surface chemistry for the reinforcement of polar rubbers, has not been well studied in literature.

In the present study, the nature of elastomer/carbon black interaction has been investigated through bound rubber measurements. For this, elastomers of different chemical natures have been utilized. The investigation also includes carbon black that has been subjected to surface oxidation.

## EXPERIMENTAL

The chlorosulfonated polyethylene (CSM) used in the present study was Hypalon-40 which contained 35% chlorine and 1% sulfur on a weight basis, and was obtained from E. I. du Pont de Nemours & Co., Inc. A chlorinated polyethylene (CPE), which contains 36 wt % chlorine (Tyrin CM 0136, Dow Corning) and a hydrogenated acrylonitrile-butadiene rubber (HNBR), containing 34.7 wt % acrylonitrile and 0.5 mol % residual double bonds (Therban 1707, Bayer) were also used.

The carbon black was a N110 (Corax N110, Degussa AG). A sample of the carbon black was surface modified by liquid phase oxidation. Typically, 50 g carbon black was treated with 800 mL of 6 mol/dm³ nitric acid for 3 h at 100°C. Thereafter the oxidized black was washed with distilled water several times and finally vacuum dried at 120°C for 24 h. The physicochemical properties of the carbon blacks are presented in Table I.

The compound formulations are given in Table II. The carbon black loading was fixed at 50 phr, and no other ingredients were incorporated. The

**Table I   Physicochemical Properties of the Carbon Blacks**

|  | N110 | Oxidized N110 |
|---|---|---|
| $N_2SA$ ($m^2/g$) | 143 | 147 |
| DBPA (mL/100 g) | 112 | 112 |
| Oxygen (%) | 1.28 | 2.97 |
| Hydrogen (%) | 0.62 | < 0.30 |
| Moisture adsorption (%) (at 79% RH and 26°C) |  |  |
| (a) in 1 h | 1.8 | 4.0 |
| (b) at equilibrium[a] | 2.9 | 6.4 |
| pH | 8.3 | 2.7 |

[a] After 20 days.

**Table II   Formulation of the Mixes**

|  | Mix Designation | | | | | |
|---|---|---|---|---|---|---|
|  | A | B | C | D | E | F |
| CSM | 100 | 100 | — | — | — | — |
| CPE | — | — | 100 | 100 | — | — |
| HNBR | — | — | — | — | 100 | 100 |
| N110 | 50 | — | 50 | — | 50 | — |
| Oxidized N110 | — | 50 | — | 50 | — | 50 |

rubber/carbon black mixtures were prepared in a Brabender Plasticorder (PLE-330). The mixing energy was held constant at approximately 3400 MJ/m³ for all compounds.

For bound rubber measurement, the rubber/carbon black mixes were conditioned for 7 days at room temperature and then cut into small pieces (1 mm³). Approximately 0.5 g (accurately weighed) of each rubber compound, loosely packed in a stainless-steel cage (150 mesh) was immersed in 300 mL toluene (or tetrahydrofuran). The solvent was renewed every 24 h. After 72 h, the cage with the bound rubber (if any) was removed from the solvent and vacuum dried at room temperature to constant weight. The bound rubber content was expressed as the weight percent of the unextracted and insolubilized polymer on the carbon black.

Fourier transform infrared (FTIR) spectra (transmission) were recorded on a Bruker IFS-66 spectrometer, with 128 scans signal averaged at a resolution of 4 cm⁻¹. Thin films for this purpose were cast from 2% (w/v) solutions in chloroform onto potassium bromide plates, followed by vacuum drying at room temperature for 2 days. Photoacoustic Fourier transform infrared spectra (PAS-FTIR) were taken with the same spectrometer by mounting an MTEC Model 200 photoacoustic attachment. Typically, PAS-FTIR spectra presented in this study were measured at 0.115 cm/s interferometer mirror velocity and 8 cm⁻¹ resolution, coadding 128 scans. All the spectra are baseline corrected. The samples for PAS-FTIR spectroscopy were degassed by keeping them under a high vacuum for at least 72 h. The sample chamber was also flushed with helium gas for 30 s prior to recording the spectra of each sample.

## RESULTS AND DISCUSSION

### Carbon Black Characterization

Table I compares the physicochemical properties of original untreated carbon black (N110) with those

of the oxidized N110 carbon black. The nitrogen surface area and the structure by DBPA of the original black remained almost unchanged by oxidation. This simply indicates that the oxidation of the carbon black by nitric acid under the present experimental conditions was mild and did not affect the porosity of the original carbon black. Similar observations were made earlier by Suzuki et al.,[11] Cotten et al.,[12] and others.[6] However, a more than twice as high oxygen content of the oxidized black indicates that the surface of the carbon black, N110, was indeed affected by the oxidation process. The oxygen in carbon blacks produces several functional groups, such as carboxyls, lactones, phenols, and quinones. The surface oxidation of carbon blacks leads to an increase in the concentration of these functional groups.[13] The increased concentration of functional groups causes a significant increase of the acidity of the carbon black. In the present investigation, the basic pH (8.3) of the original black has changed to an acidic pH (2.7) by oxidation. But it is not clear why almost all furnace blacks are basic in nature, even though they contain acidic functional groups (e.g., phenolic hydroxyls, carboxyls etc.). However, these carbon blacks can be titrated with strong bases in both aqueous[14] and nonaqueous mediums,[8,15] confirming the existence of acidic groups. It is, therefore, understandable that oxidized carbon blacks show an increased reactivity toward bases.[8] Furthermore, the oxygenated functional groups are also responsible for the moisture-adsorption properties of carbon blacks.[16,17] The moisture adsorption by the oxidized N110 carbon black is much higher than by the original carbon black (Table I). Consequently, it appears likely that the oxidized carbon black rather than the untreated carbon black possesses a better affinity for polar molecules.

## Bound Rubber

### *Effect of Polarity of Polymers*

It is generally agreed that bound rubber, the percentage of polymer defying extraction by a good solvent in an elastomer/filler mix, is a valuable measure of polymer/filler interaction. But there has never been any widespread agreement on the nature of the bonds involved in bound rubber. The polymer/filler interaction leading to the formation of bound rubber are dependent mainly on the physicochemical properties of the carbon blacks and the chemical structure of the polymers. Again, all the three elastomers used in the present work (i.e., CSM, CPE, and HNBR) are saturated or nearly saturated. The

polarity of the elastomers, in such cases, appears to be an important factor for polymer/filler interaction. Wang et al.,[18] in their investigation of adsorption of polar probes on carbon black surfaces by inverse gas chromatography (IGC), demonstrated that the —CN groups of nitriles interacted more strongly with the black surface through specific interaction than did the double bonds of normal alkene probes. This behavior is attributed to the considerably higher polarity of —CN groups and to their ability to form hydrogen bonds with the black surfaces.[18]

The bound rubber contents of the compounds are listed in Table III. The CSM/carbon black compounds have rather high bound rubber contents compared to the HNBR and CPE compounds. In fact, HNBR compounds do not even give any coherent mass when extracted with tetrahydrofuran. If bound rubber is indeed a measure of polymer/filler interaction, the interaction between HNBR or CPE and carbon black is less pronounced than between CSM and carbon black. However, it was also observed that the bound rubber levels of NR and NBR, with the same carbon black (N110) at the same loading, were 46 and 24%, respectively (extracting solvent was toluene). With regard to polarity, the elastomers show the following trend: NBR > HNBR > CSM ≥ CPE > NR. This means that no apparent correlation exists between bound rubber and the polarity of polymers. The results obtained from bound rubber measurements thus contradict the IGC data. There are two possible explanations for this discrepancy. Firstly, the IGC method does not consider the practical situation, namely, the structural changes of both fillers and polymers dur-

**Table III    Bound Rubber Content**

| | | Bound Rubber Content (%) | |
| | | N110 | Oxidized N110 |
|---|---|---|---|
| Elastomer | Solvent | | |
| CSM | toluene | 19 ± 0.5 | 33 ± 0.5 |
| | tetrahydrofuran | 18 ± 0.5 | 31 ± 0.5 |
| CPE | tetrahydrofuran | 7 ± 0.5 | 9 ± 0.5 |
| HNBR | tetrahydrofuran | —[c] | —[c] |
| NBR[a] | toluene | 24 ± 0.5[d] | 25 ± 0.5[d] |
| | tetrahydrofuran | 24 ± 0.5[d] | 24 ± 0.5[d] |
| NR[b] | toluene | 46 ± 0.5[d] | 54 ± 0.5[d] |

[a] Krynac 34.50 (contains 34 wt % acrylonitrile), Polysar.
[b] ISNR-5, Indian Rubber Research Institute.
[c] No coherent gel.
[d] Author's unpublished data.

ing mixing. In fact, the primary structure of carbon blacks is subjected to a significant breakdown during mixing, which thus creates new active surfaces for elastomer/filler bonding.[19-21] Furthermore, unsaturated polymers are susceptible to mechanochemical scission during mixing. Macroradicals thus formed seem to react with carbon black to produce carbon gel or bound rubber.[2,22] Second, the measurement of elastomer/filler interaction via bound rubber may be handicapped by multiattachment of rubber molecule on the black surface, giving anomalous results.

Earlier Kraus and Dugone,[23] in their study of adsorption-desorption of typical rubbers on carbon black from solution, found that the adsorption process is accompanied by sufficient irreversibility, leading to the formation of some bound rubber in almost all cases. Adsorption of rubbers from hydrocarbon solution on carbon blacks is proportional to the external surface area of the black, independent of the chemical nature of the black and the polymer.[23] The same conclusion was drawn by Wade et al.,[24,25] with microcalorimetry. It was noted that the integral heat of immersion per unit surface area of the black was practically constant, hardly influenced by carbon black type and the nature of hydrocarbon solvent (ranging from $n$-decane to liquid rubbers). From the above observations, it follows that elastomer/carbon black interaction is essentially a physical phenomenon, analogous to wetting of an exceedingly high-energy surface with a solvent of relatively low surface energy. This then implies that the dispersive component of surface energy, $\gamma_s^d$, of the carbon black is the dominant factor while the chemical nature of the elastomer is of the least importance. If this concept is accepted, a marked dependence of elastomer/filler interaction on the nature of the elastomer, as observed in bound rubber measurement, cannot have any satisfactory interpretation. For instance, the supposed strong physical and specific interactions in HNBR/carbon black system, contrary to our expectation, is not reflected in bound rubber. Even if the concept of multiattachment is taken into account, there is also no clue why HNBR, in particular, would give multiattachment with carbon black. Summing up all the points, it seems logical to conclude: Bound rubber formation is essentially a chemical process involving primary bond formation between elastomer and carbon black.

### Effect of Carbon Black Surface Functionalities

The role of the functional groups on carbon black surface in elastomer/filler interaction is not clear. It is generally conceived that oxygen containing groups on carbon blacks are detrimental to reinforcement.[6,26,27] Nevertheless, a number of investigations[6-9] showed that oxidized carbon blacks enhanced the bound rubber formation. The present work is in agreement with the above observation (see Table III). As the morphology of the carbon black remained unchanged by the oxidative treatment (Table I), its dispersive component of the surface energy, $\gamma_s^d$ is also not affected.[18] This means that the change in bound rubber contents with surface treatment is not attributed to physical forces. Again, as observed by Serizawa et al.,[6] carbon blacks on surface oxidation impart higher segmental mobility to both the tightly and loosely bound rubber phases. This does not necessarily mean a loss of reinforcement as the higher segmental mobility of bound polymers was compensated by the higher volume fraction of both the phases.[7] Hess et al.,[26] however, observed that oxidized carbon black-filled SBR vulcanizates had lower modulus values as compared to unoxidized black filled vulcanizates. This is probably not related to the reinforcing efficiency of the carbon blacks. The differences in modulus values in such cases are attributed to differences in crosslink densities because the acidity of the oxidized blacks is known to reduce the crosslinking efficiency of both the peroxide[28] and sulfur/accelerator[12] crosslinkers. Obviously, there is no definite proof that oxidized carbon blacks are less reinforcing.

### Elastomer/Carbon Black Chemical Reactions

From the previous discussion, it appears that bound rubber formation is essentially a chemical process involving reactions between elastomer and carbon black. Although the true nature of the chemical reaction remains obscure, the general preference is for a free radical reaction between elastomer macroradicals and carbon black. It was postulated that elastomer free radicals, resulting from either chain scission[22] or hydrogen abstraction,[29] attach themselves to the carbon black surface which is a free radical acceptor. In this way almost all unsaturated polymers are capable of being linked with carbon blacks. On the contrary, the inert backbone of saturated polymers such as HNBR and CPE is highly resistant to chain scission and hydrogen abstraction. Moreover, the —CN and secondary chloride groups are sufficiently stable and hence they do not tend to react with a carbon black surface. With CSM the situation is completely different. In the molecular chains there exists a small quantity of sulfonyl chloride groups which make the elastomer highly reactive, particularly to hydroxylated compounds.[30,31] So it is quite logical to expect a reaction between the hydroxyl groups on a carbon black surface and the

— $SO_2Cl$ groups of CSM. The reaction may occur in the following fashion to lead to the formation of sulfonate linkages:

$$CB. — ) — OH + {\sim}CH{\sim} \rightarrow$$
$$\begin{array}{c} | \\ SO_2Cl \end{array}$$

$$CB. — ) — O — O_2S — CH{\sim} + HCl \quad (1)$$
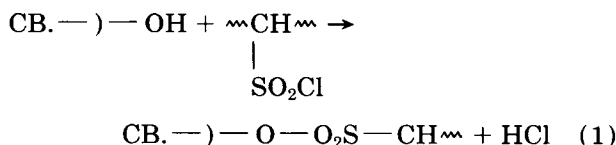
Furthermore, it is well known[30,31] that the — $SO_2Cl$ groups of CSM in the presence of free radicals undergo a decomposition reaction to generate polymer free radicals:

$$RSO_2Cl + X^{\bullet} \rightarrow RSO_2^{\bullet} + XCl \quad (2a)$$

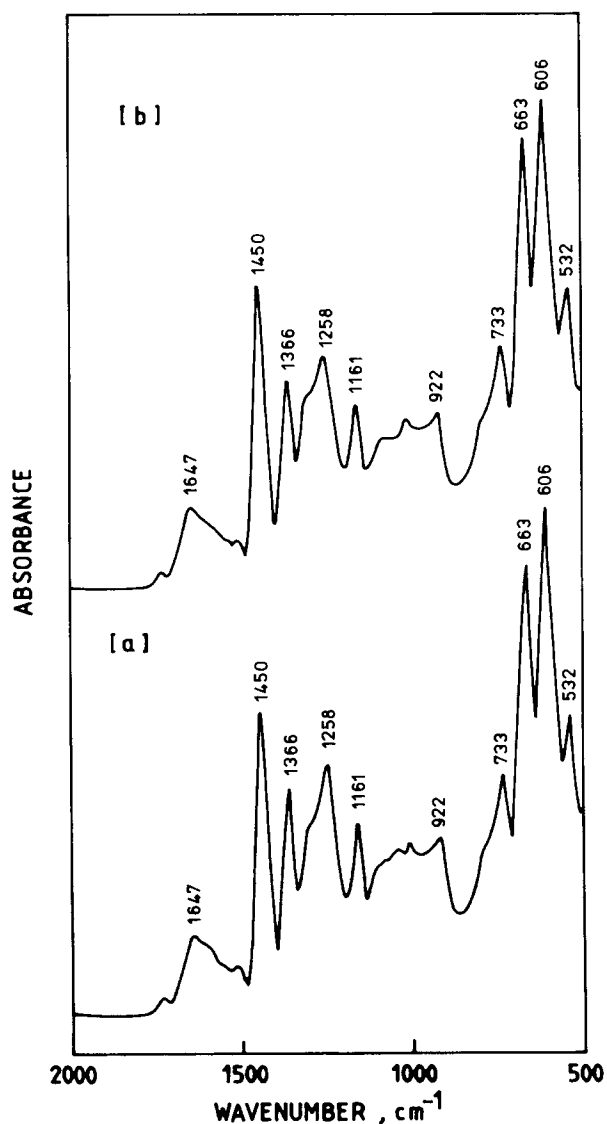$$RSO_2^{\bullet} \rightleftharpoons R^{\bullet} + SO_2 \quad (2b)$$



**Figure 1**  FTIR transmission spectra of (a) pure CSM; and (b) extracted unbound rubber from CSM/N110 mix.

**Table IV    Relative Absorbance[a] of the Infrared Bands at 1161 and 1366 cm⁻¹ of CSM in Figure 1**

|  | Pure CSM | Extracted (Unbound) CSM |
|---|---|---|
| $A_{1161}/A_{1450}$ | 0.305 | 0.245 |
| $A_{1366}/A_{1450}$ | 0.490 | 0.415 |

[a] Band at 1450 cm⁻¹ taken as internal reference.

(where $X^{\bullet}$ indicates a free radical

and $R^{\bullet}$ is the polymer radical)

The free radicals thus formed are likely to combine with the free radicals present on the carbon black surface. Here, the carbon black surface may play a double role: In the first place, it can act as a free radical source to promote the decomposition of $SO_2Cl$ groups, thus producing polymer free radicals. Second, as a free radical acceptor, it is able to combine with the polymer free radicals. This type of dual function of carbon blacks was observed by Kraus et al.,[32] Donnet et al.,[33,34] and many others.[35–38] These authors associated the quinone or phenolic hydroxyl groups on the surface of carbon blacks with the primary free radical sites. So, as an alternative to sulfonate linkages, the free radical coupling between the CSM macroradicals and quinone or phenoxy radical sites on carbon blacks may lead to ether type bonds, e.g., CB. — ) — O — CH$\sim$.

Figure 1 shows the FTIR spectrum of pure CSM and that of unbound rubber extracted from CSM/ N110 compound. The two strong absorption bands at 1161 and 1366 cm⁻¹ are characteristic of — $SO_2Cl$ groups of CSM. These peaks are assigned to symmetric and asymmetric stretching modes of $SO_2$, respectively.[39] The corresponding bands of extracted unbound rubber occur at the same positions, but their intensity of absorption is somewhat diminished (Table IV), indicating a loss of the — $SO_2Cl$ moieties. This observation can be interpreted on the basis of the following side reaction.[30,31]

$$\sim CH_2 — CH\sim \rightarrow$$
$$\begin{array}{c} | \\ SO_2Cl \end{array}$$

$$\sim CH{=}CH\sim + SO_2 + HCl \quad (3)$$
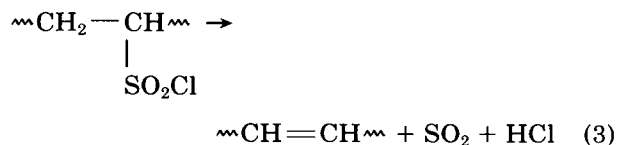
The resulted unsaturated species are generally inactive and therefore form the extractable unbound bulk polymer in the elastomer/carbon mixture. For good elastomer/carbon black bonding, it is essential
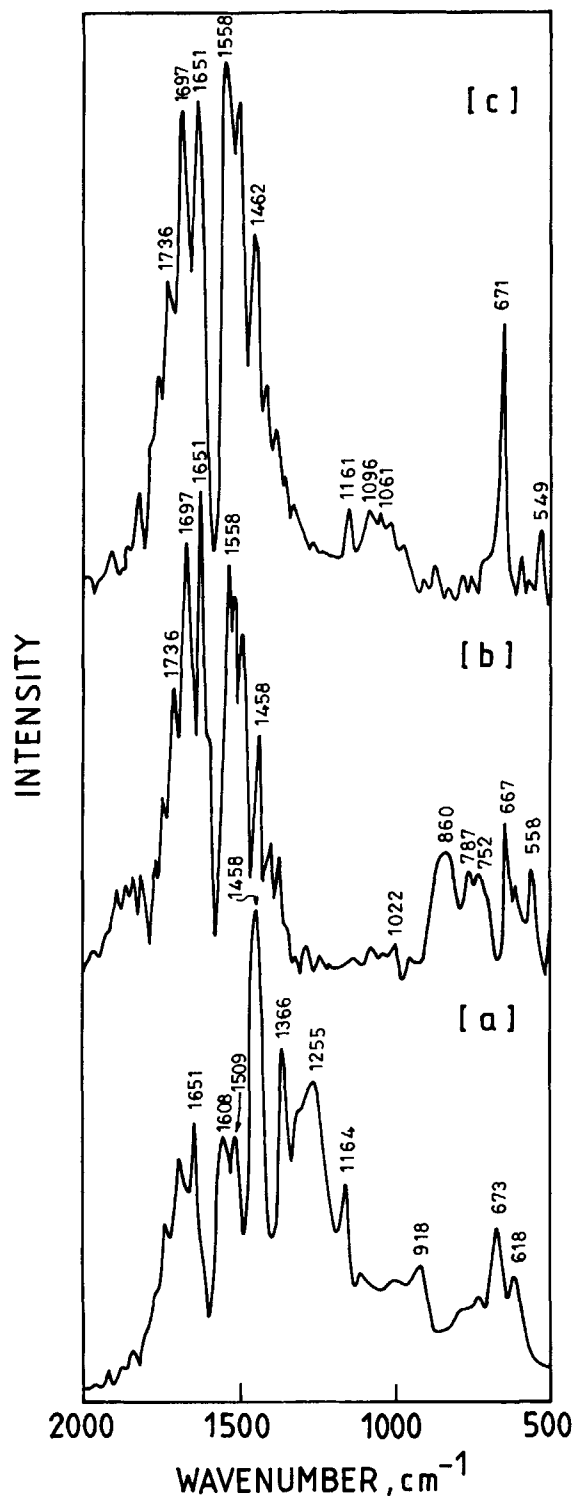
**Figure 2**  FTIR-photoacoustic spectra of (a) pure CSM; (b) carbon black N110; and (c) CSM/N110 compound.

to suppress this undesired reaction. The oxidized carbon black provides a higher concentration of the surface functional groups to be available for the reactions with the —SO$_2$Cl groups, thereby discour-

aging the decomposition of the latter. This may be the reason why the oxidized carbon black exhibits a higher bonding capacity. Alternatively, if the CSM/carbon black reaction is free radical in nature, the better bonding capacity of the oxidized carbon black may arise from its greater affinity for free radicals.[40]

Figure 2 shows the PAS-FTIR spectra of pure CSM, the carbon black N110, and the CSM/N110 compound. A number of bands in the 1800–1680 cm$^{-1}$ region in the spectrum of N110 (Fig. 2b) confirm the presence of different carbonyl functionalities which may include carboxyl, lactone, and quinone. The band at 1651 cm$^{-1}$ is characteristic of aromatic double bonds in the carbon black. The spectrum of the carbon black filled CSM compound (Fig. 2c) retains all the characteristic bands due to the carbon black. However, there occur several additional bands in the 1100–1000 cm$^{-1}$ region which do not correspond either to CSM or to the carbon black. Although the specific assignments of these new peaks are not known at present, their presence possibly indicates the formation of new species due to polymer/filler reactions.

## CONCLUSIONS

The oxidation of carbon black surface by nitric acid improves its surface activity, as evidenced by the moisture adsorption and the bound rubber measurements. Bound rubber formation is principally dependent on the ability of both the elastomer and the carbon black to form the primary chemical bonds between them. Bound rubber is thus primarily an elastomer grafted carbon black. There is of course a little contribution from physical adsorption of polymer on carbon black, but this effect is almost constant for all rubbers, irrespective of their chemical natures.

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