

# Reinforcement of Epoxidized Natural Rubber by Carbon Black: Effect of Surface Oxidation of Carbon Black Particles

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## SYNOPSIS

Epoxidized natural rubber (ENR) reacts with surface oxygen groups of carbon black. The higher the concentration of these groups, the higher the intensity and the extent of reaction and the better the reinforcing ability of the black. Oxidized furnace blacks and channel blacks, which are known to have high quantities of oxygen functional groups, are thus more reinforcing than are the conventional furnace blacks, particularly in the case of black-filled epoxidized natural rubber. © 1993 John Wiley & Sons, Inc.

## INTRODUCTION

Surface chemistry of carbon black fillers has attracted the attention of scientists and technologists for a long time.<sup>1-3</sup> The carbon black filler contains a large number of other elements, such as oxygen, hydrogen, nitrogen, and sulfur. The surface functional groups produced by the heteroatoms include carbonyls, lactones, phenols, and quinones.<sup>4-9</sup> Moreover, there are reports on the occurrence of such groups as ketones,<sup>10</sup> hydroquinones,<sup>11</sup> ethers,<sup>9</sup> and pyrones.<sup>12,13</sup> Hydrogen is present partly in the surface oxygen functional groups (—COOH, —OH, etc.) and partly combined with the carbon atoms. Surface hydrogen is chemically reactive.<sup>14-16</sup> The nature of the sulfur and nitrogen groups has not yet been conclusively established.

It is generally believed that the surface energy of blacks is of much greater importance than is their chemical nature with regard to the reinforcement of filled elastomers.<sup>3,17,18</sup> But there is no denying that the chemical interaction between carbon black and elastomer, if present, contributes significantly to the reinforcement process.<sup>19</sup> There are differences of opinion as to which particular surface groups are responsible for the formation of carbon black-elastomer attachments. Papirer and co-workers<sup>16,20</sup> observed a substantial exchange of hydrogen between

carbon black and elastomer. In recent years, Donnet<sup>21</sup> and Ayala and co-workers<sup>22-24</sup> advocated the importance of carbon-bound hydrogen to carbon black surface activity. The oxygen functional groups, on the other hand, play an important role in the reinforcement of elastomers of low unsaturation. Gessler and co-workers<sup>25-29</sup> found that oxidized furnace blacks and channel blacks, which are known to have high quantities of carboxyl groups, undergo a strong chemical interaction with butyl rubber when the rubber-black mix is subjected to heat treatment. In recent years, Asai et al.<sup>30</sup> asserted that the oxidative treatment of carbon black enhanced the reinforcement effect of carbon black even in the natural rubber-carbon black system.

The measurement of surface energies of carbon blacks by inverse gas chromatography by Papirer et al.<sup>31</sup> showed that the surface oxidation of carbon blacks does not significantly change the dispersive component of surface energy,  $\gamma_s^d$ . The oxidized blacks, on the other hand, show a higher affinity for polar probes. This is attributed to their high concentration of oxygen groups that are polar sites by nature. Furthermore, Wang et al.<sup>18</sup> showed that the rubber-carbon black interaction depends not only on carbon black surface energies, but also on the structure of the elastomers. Polar rubbers (e.g., NBR) show stronger interaction with blacks than do general purpose olefinic rubbers.<sup>18</sup>

It is, therefore, worth studying the interaction of polar carbon blacks (channel blacks, oxidized furnace blacks) with polar rubbers. The present study investigated the role of chemical interaction in the

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**Table I Formulation of the Mixes (Not Containing Curative) and Percent Bound Rubber and Volume Swelling of Rubber (in Swollen Gel)**

	Mix No.							
	1	2	3	4	5	6	7	8
ENR-50	100	100	100	—	—	—	—	—
ENR-25	—	—	—	100	100	100	—	—
NR	—	—	—	—	—	—	100	100
N121	50	—	—	50	—	—	50	—
Oxidized N121	—	50	—	—	50	—	—	50
S301	—	—	50	—	—	50	—	—
Bound rubber <sup>a</sup> (%)	17	24	20	26	35	31	41	48
Volume Swelling <sup>b</sup> (%)	860	500	650	1050	675	800	— <sup>c</sup>	— <sup>c</sup>

<sup>a</sup> Average of four test results (standard deviation < 0.5 in all cases).

<sup>b</sup> With heat-treated samples.

<sup>c</sup> Not performed.

reinforcement of epoxidized natural rubber by carbon blacks.

## EXPERIMENTAL

### Materials

Epoxidized natural rubbers (Epoxyrene-25 and Epoxyrene-50, designated as ENR-25 and ENR-50, respectively, from Kumpulan Guthrie Berhad, Malaysia) contain 25 and 50 mol % oxirane rings, respectively. The natural rubber (NR) used was ISNR-5 (Rubber Research Institute of India, India).

The rubber-grade furnace black of N121 type and the corresponding oxidized black used in the present study were obtained from Columbian Chemicals Co., U.S.A. The surface area and structure of these blacks are almost identical ( $N_2SA$ : 127 m<sup>2</sup>/g, and  $DBPA$ : 132 mL/100 g). A channel black, S301 ( $N_2SA$ : 120 m<sup>2</sup>/g, and  $DBPA$ : 113 mL/100 g), was also used.

### Compounding

Each of the three carbon blacks was mixed with the rubbers according to the formulations given in the Table I. Mixing of carbon black and rubber was carried out at room temperature in a Brabender Plasticorder (Model PLE-330) equipped with a cam-type mixing head at a constant total energy input for all compounds (approximately 3400 MJ/m<sup>3</sup>). The curative was added to the black-rubber masterbatch on an open mill at a temperature not exceeding 60°C.

### Bound Rubber Measurement

The rubber-carbon black mixes were kept at room temperature for 2 days and then cut into small pieces, approximately 0.5 g of which was placed into a stainless-steel cage (150 mesh size) and immersed in a sufficiently large amount of toluene (300 mL). The extraction was carried out at room temperature for 72 h. The cage with the bound rubber was then removed from the solvent and vacuum-dried at room temperature to a constant weight. Bound rubber content (BRC) was expressed as the weight percent of insolubilized polymer remaining on the black.

### Rheometric Study

Rheometric studies of the rubber-carbon black mixes (with and without curative) were carried out with a Monsanto Moving Die Rheometer (MDR-2000) operated at 170°C with a 0.5° arc of oscillation.

### Heat Treatment and Molding

The heat treatment of rubber-carbon black mixes not containing curative was carried out by molding at 170°C for 60 min under a pressure of 10 MPa using a laboratory press. The rubber mixes containing curative (Table II) were vulcanized by molding at 170°C to optimum cure times under 10 MPa pressure. The uncross-linked samples from rubber-black mixes (without curative) were prepared by molding at 80°C for 2 min.

**Table II Formulation of the Mixes Containing Curing Agent**

	Mix No.	
	1'	2'
ENR-50	100	100
N121	50	—
Oxidized N121	—	50
Dicumyl peroxide	1	1

### Swelling

Swelling measurements were performed in toluene at room temperature according to the method described by Ellis and Welding.<sup>32</sup>

### Testing

Stress-strain properties were measured using a Zwick (Model 1445) universal testing machine as per ASTM D 412-87 (Method A). Dynamic mechanical properties were measured using a Rheovibron (Model DDV-III-EP, Orientec Corp., Japan) at a double-strain amplitude of 0.166% and a frequency of 3.5 Hz in the temperature range of  $-100^{\circ}\text{C}$  to  $+150^{\circ}\text{C}$  with a  $2^{\circ}\text{C min}^{-1}$  linear rise of temperature.

## RESULTS AND DISCUSSION

### Bound Rubber

The formation of bound rubber provides information concerning rubber-filler interactions that are due mainly to physical adsorption and chemisorption.<sup>33-35</sup> In the present investigation, the bound rubber level of NR with N121 is significantly higher than for the other two elastomers (Table I). The next highest is ENR-25, followed by ENR-50. This observation is in line with the general belief that the higher the unsaturation level of the rubber the higher the formation of bound rubber.<sup>35</sup> It is, however, noteworthy that both oxidized N121 and channel black produce a substantial increase in bound rubber over that produced by N121. This is in agreement with the observations made by Serizawa et al.<sup>36</sup> and Asai et al.<sup>30</sup> in reference to the NR-carbon black system. They found that the incorporation of surface-oxidized carbon black into NR produced a significant increase in bound rubber,

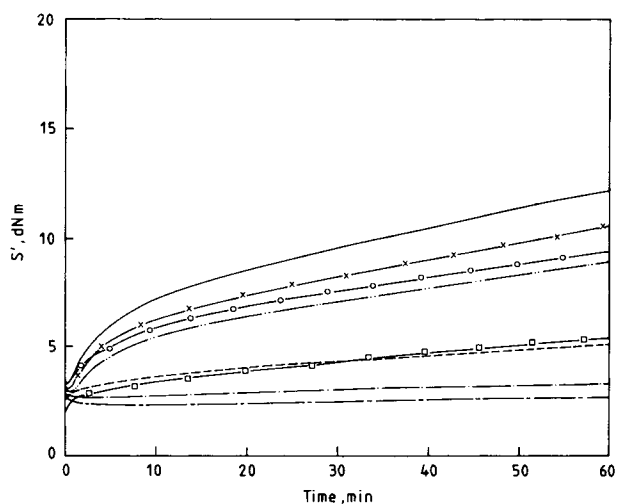
which was supposed to be due to strong interaction between carbon black and rubber molecules.

### Rheometric Studies

Both epoxidized natural rubber (ENR) and oxidized carbon black have reactive sites: They are expected to react at elevated temperatures. To assess the chemical reaction between rubbers and carbon blacks, a Monsanto Moving Die Rheometer was conveniently employed. Figure 1 shows the rheographs of rubber-carbon black mixes (without curative) at  $170^{\circ}\text{C}$ . The increase in rheometric torque with time is attributed to either chemical bonding of the elastomer phase to the filler surfaces or rubber-rubber bonding or both. It is also apparent that (a) oxidized N121 and channel black (S301) cause a higher extent of chemical interaction than does the untreated black (N121) and (b) an increase in epoxy content (ENR-50 vs. ENR-25) enhances the extent of reaction. In fact, NR shows practically no rise in rheometric torque with all the three blacks. This implies that the reaction between functional groups on carbon black and elastomer is playing the key role in increasing the rheometric torque.

### Dynamic Properties

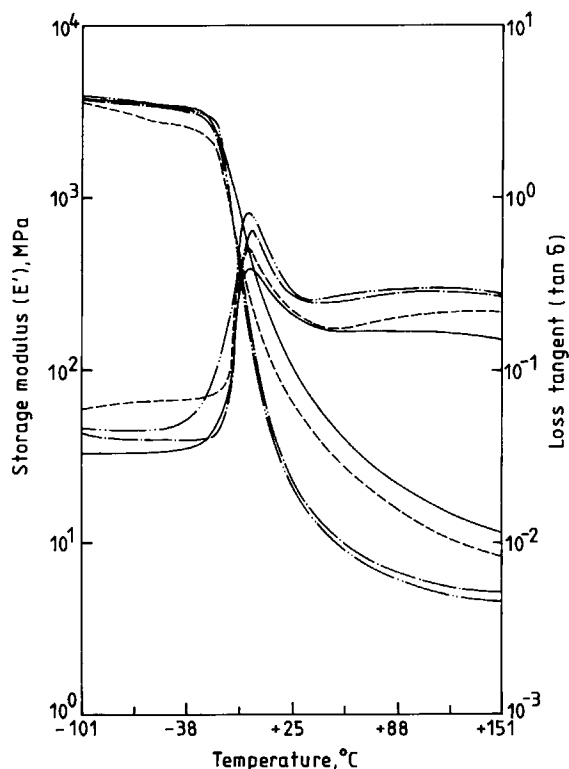
The bound rubber measurement and rheometric study suggested that the comparatively weak polar



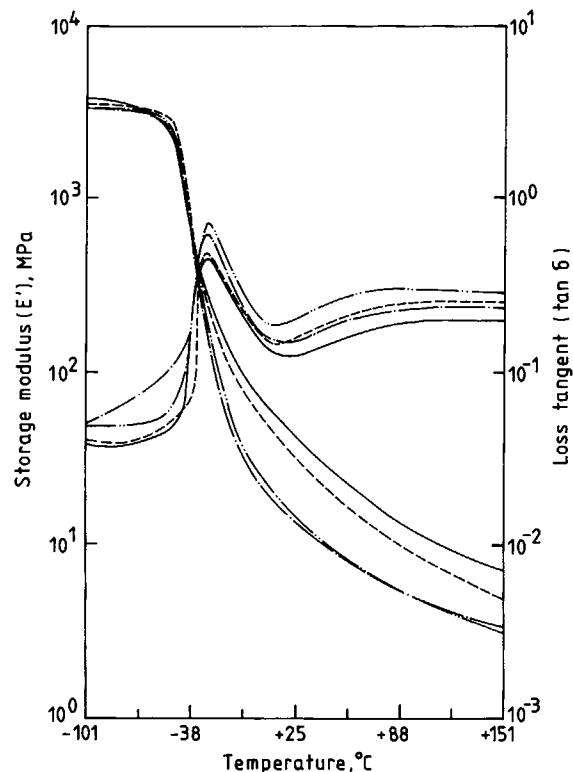
**Figure 1** Rheographs of rubber-carbon black mixes (without curative): (a) (—) ENR-50/oxidized N121; (b) (—□—) ENR-50/N121; (c) (—○—) ENR-25/oxidized N121; (d) (---) ENR-25/N121; (e) (—×—) ENR-50/S301; (f) (—·—) ENR-25/S301; (g) (—□—) NR/oxidized N121; (h) (---) NR/N121.

attachments of rubber and carbon black (in addition to strong physical force) are replaced by chemical bonds at elevated temperatures. The effect of chemical interaction on reinforcement can be better understood from the dynamic mechanical studies. Figures 2 and 3 show the temperature dependence of the dynamic storage moduli of ENR-black systems. Obviously, the samples molded for prolonged times at elevated temperatures show markedly higher modulus values, in the rubbery region, compared to the samples without heat treatment. Although the ENR and unoxidized black system show a degree of response to heat treatment as evidenced by the enhancement of storage modulus, the improvement is much higher in the case of ENR-oxidized black. On the contrary, N121 and oxidized N121 give comparable modulus values in the absence of heat treatment.

As the modulus of cross-linked elastomer is proportional to the cross-link density, according to statistical theory of rubber elasticity,<sup>37</sup> the enhancement of low-strain dynamic modulus by heat treatment is thus attributed to the increase in rubber-



**Figure 2** Temperature dependence of the dynamic properties of (a) (—) ENR-50/oxidized N121, heat-treated, (b) (- · -) ENR-50/oxidized N121, without heat treatment, (c) (- - -) ENR-50/N121, heat-treated, and (d) (- · · -) ENR-50/N121, without heat treatment.



**Figure 3** Temperature dependence of the dynamic properties of (a) (—) ENR-25/oxidized N121, heat-treated, (b) (- · -) ENR-25/oxidized N121, without heat treatment, (c) (- - -) ENR-25/N121, heat-treated, and (d) (- · · -) ENR-25/N121, without heat treatment.

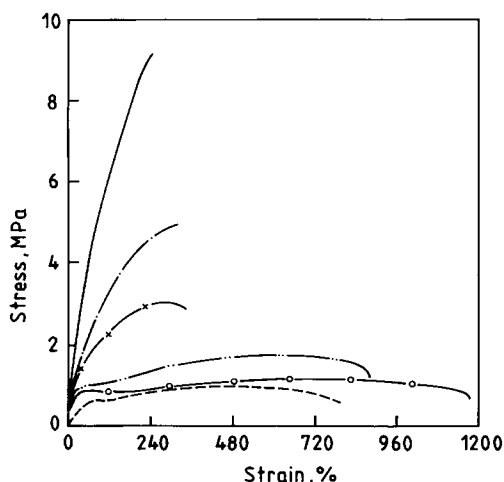
filler attachments, which behave as cross-links. The increase of effective cross-link density induced by heat-treatment is also responsible for the decrease of loss tangent ( $\tan \delta$ ) of the rubber-filler stocks (Figs. 2 and 3). The reduction of  $\tan \delta$  by heat treatment is of much significance because  $\tan \delta$  is a measure of energy loss (or hysteresis loss) under a constant energy deformation.<sup>38,39</sup> The improvement of loss properties due to the increase in effective cross-links can be interpreted in the following way<sup>39</sup>: The higher the cross-link density, the lower the concentration of dangling chain ends and of untrapped entanglements. As a result, the friction generated by dragging these species through the polymer is obviously less. Thus, the higher cross-link density causes lower friction and lower hysteresis loss. Lastly, it should be noted that the ENR-oxidized black system shows a much improved hysteresis property than that of the ENR-nonoxidized black system as a consequence of comparatively higher polymer filler interactions, which can be further improved by heat treatment.

### Stress-Strain Properties

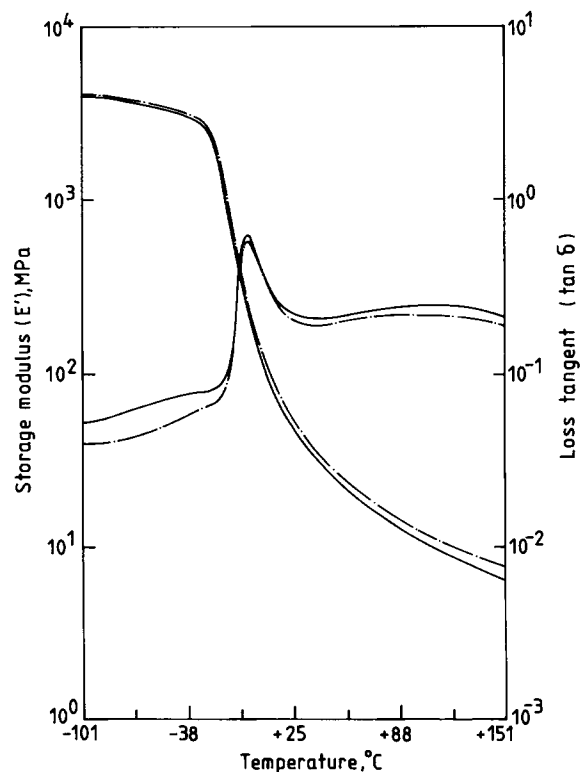
The stress-strain properties, showing the effect of heat treatment on modulus and ultimate properties, are presented in Figure 4. In uniaxial extension, elongation to break and high-strain moduli are dependent on the cross-link density of the elastomer.<sup>40</sup> It is needless to say that the severalfold increase of 100 and 300% moduli, as well as tensile strength in the case of ENR-oxidized black (as well as ENR-channel black), by heat treatment is due to the cross-linking of rubber phase by the filler. Compared to oxidized N121, nonoxidized black is less effective toward the formation of additional bonding with ENR at elevated temperature, as reflected in the stress-strain properties (Fig. 4). As both N121 and oxidized N121 have identical surface area and structure, the better reinforcement of ENR by oxidized black is unmistakably attributed to oxygen surface groups and these groups react with ENR. A study on the mechanism of such reactions is now underway.

### Comparison of N121 and Oxidized N121 in Conventional ENR Vulcanizates

After having investigated the effect of surface oxidation of the black on rubber-filler interaction, it would be interesting to compare these two blacks in ENR that is cross-linked with conventional curing



**Figure 4** Stress-strain properties of (a) (—) ENR-50/oxidized N121, heat-treated and (b) (— · —) ENR-50/oxidized N121, without heat treatment, (c) (— × —) ENR-50/N121, heat-treated, (d) (— o —) ENR-50/N121, without heat treatment, (e) (— • —) ENR-50/S301, heat-treated, and (f) (---) ENR-50/S301, without heat treatment.

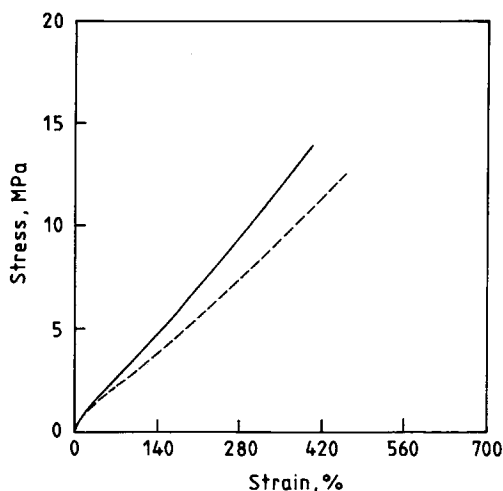


**Figure 5** Temperature dependence of the dynamic properties of peroxide-cured (a) (— · —) ENR-50/oxidized N121 and (b) (—) ENR-50/N121.

agents. Such an investigation was carried out using the compound formulations shown in Table II. As expected, oxidized black-filled ENR vulcanizate gives a higher cross-link density as checked by swelling studies. The additional cross-links are understandably due to covalent rubber/filler bonds that were formed at vulcanization conditions. Accordingly, it gives comparatively higher dynamic storage modulus, lower  $\tan \delta$  (Fig. 5), higher high-strain modulus (100 and 300% moduli), and higher tensile strength (Fig. 6).

### CONCLUSIONS

1. ENR reacts with carbon black, particularly with oxidized carbon black. The intensity and the extent of reaction depend on the epoxy content of ENR as well as the concentration of surface oxygen functional groups of carbon black.
2. Reaction of ENR and oxidized black is equivalent to cross-linking of ENR by the filler.



**Figure 6** Stress-strain properties of peroxide-cured (a) (—) ENR-50/oxidized N121 and (b) (---) ENR-50/N121.

- The rubber-carbon black reaction gives much improved dynamic and physical properties. Accordingly, oxidized furnace blacks or channel blacks are more reinforcing than are ordinary furnace blacks, particularly in the case of ENR.

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