

# 1,3,5-Trihydroxy Benzene as a Surface Modifier of Carbon Black and Its Effect on the Filler–Rubber Interaction

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**ABSTRACT:** A surface-modified rubber-grade carbon black has been prepared by treating it with 1,3,5-trihydroxy benzene (phluroglucinol) in aqueous solution at different molar concentrations. This modified carbon black has been used as one of the compounding ingredients with natural rubber. An attempt has been made to

establish a concentration optimum for the modifier. Improved physicomachanical properties like hardness, heat buildup, hysteresis loss, and improved dynamic mechanical properties are observed for the compounded rubber. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 87: 2272–2278, 2003

## INTRODUCTION

Carbon black, when used as a filler in polymeric substances, has a range of physical and chemical attributes (viz., particle size, surface area, structure, surface activity, etc.). It can also change elastomer properties in different ways and to different extents. While compounding carbon black with the base polymer, proper selection of polymers, suitable quality of carbon black grade, its level of combination, and the accurate vulcanization system to give a rubber compound of the desired properties at a competitive cost are essential.

The objective of the present investigation is to explore the possibility of imparting improved properties with respect to both the surface chemistry of carbon black and of the associated polymer (in this case natural rubber) by the addition of a suitable chemical. The chemical to be selected should have the potential to react with the carbon black surface components and/or with the base polymer.

It is known that the presence of heteroatoms is expected to modify the surface behavior of carbon black, which ultimately determines their application in the rubber, plastics, and paints industries. The surface is characterized by dispersive and polar components of surface energy. Extensive literature survey shows that carbon black, having its surface modified by Si-69,<sup>1</sup> aliphatic dihydric and trihydric alcohol,<sup>2,3</sup> imparts improved hysteresis and improved abrasion

resistance properties at low and high temperatures compared to the native carbon black. It is reported that surface modification by a silane-coupling agent leads to lowering in reinforcement.<sup>4</sup> It is also reported that carbon black with a phenolic plant product<sup>5</sup> gives flex crack growth resistance. Carbon black modified with vegetable oil<sup>6</sup> shows high tensile strength and elongation properties, low abrasion, and hardness. Ganguly et al., in an attempt to study the effect of meta dihydroxy benzene,<sup>7</sup> a surface modifier, have observed that there has been an improvement in the properties of curing characteristics, modulus, and tensile strength. Taking cue from this investigation, in the present study an attempt has been made to use 1,3,5-trihydroxy benzene<sup>8</sup> as a surface modification agent. It is expected that the three hydroxyl groups of the above compound in a symmetric position would act as better surface modification agents, thus imparting improved compound properties.

## EXPERIMENTAL

### Materials used

The natural rubber (RMA-1X) had a moisture content of 1%, ash content of 0.4%, specific gravity of 0.9, and Mooney viscosity (ML, 1+4 at 100°C) of 60. Zinc oxide (E. Merck) and sulfur (Qualigen) were of laboratory reagent grade; accelerator N-oxydiethylbenzthiazyl sulfenamide (NOBS) and peptizer pentachlorothio-phenol (PCTP) were from ICI (India) Ltd. The carbon black (Orient Black N330) was supplied by Phillips Carbon Black Limited, India. The phluroglucinol (E. Merck) was of laboratory grade.

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**TABLE I**  
**Sample Identifications and Their Compositions**

Sample A	Sample B	Sample C	Sample D
500 g black (N330) and 50 cc 0.01% Phluroglucinol Solution in water	500 g Black (N330) and 50 cc 0.1% Phluroglucinol Solution in water	500 g Black (N330) and 50 cc 1.0% Phluroglucinol Solution in water	500 g black (N330) without any additive

### Preparation of modified carbon black sample

Three different strengths of aqueous phluroglucinol solution were made and sprayed over the dryer discharge product of carbon black sample (temperature 17°C) with uniform stirring to ensure proper mixing. Details of the composition of the carbon black and the phluroglucinol solution along with the respective sample identification are given Table I. It was ensured that the samples were moisture free before mixing. The untreated carbon black had a di-*n*-butyl phthalate (DBP) absorption value (ASTM D2414) of 102.5 mL/100 g, crushed DBP absorption value (ASTM D3493) of 87.5 mL/100 g, iodine number (ASTM D1510) of 83.6 mg/g, cetyl trimethyl ammonium bromide (CTAB) (ASTM D3765) of 82.4 m<sup>2</sup>/g, and tint strength (ASTM D3265) of 103 % international tint reference black (ITRB). The colloidal properties were found to be unaltered before and after the addition of the chemical.

### Compound formulation

Each of the compounds contained NR(RMA-1X): 100.0 phr; carbon black: 50.0 phr; PCTP: 0.15 phr; NOBS: 0.65 phr; ZnO: 3.00 phr; sulfur: 2.50 phr; stearic acid: 1.50 phr. The PCTP was used as a peptizer to facilitate the mixing process.

Mixing was carried out in a laboratory two-roll mill (6 inch by 12 inch) at a friction ratio of 1:1.4, a front and back roll speed of 24 and 33 rpm, respectively, and a temperature of 70°C. Care was taken for complete dispersion of filler and the same time (17 min) was allocated for all the mix to ensure same level of polymer–filler interaction. The compounds were identified according to the identification of the carbon blacks (Table I).

All the compounds were given a maturation time of 24 h at 25°C and were cured at their respective equivalents of their rheometric optimum cure times at 145°C in a steam-heated hydraulic press.

### Rheometry

After maturation of 24 h, rheometer data was obtained in a Monsanto R-100 model at ±3° arc and 100 Range scale at temperatures of 140, 160, and 180°C.

### Mechanical properties

Dumbbell-shaped samples were prepared from cured sheets that were subsequently tested for modulus, tensile strength, elongation, and tear energy according to ASTM D412-51 in an Instron 6021 Universal Testing Machine at 27°C at a crosshead speed of 500 mm/min. A bench thickness gauge measures the thickness of the samples.

### Aging analysis

Aging analysis was carried out according to ASTM D573. The test samples were exposed to aging in a hot air oven at 70°C for a total time of 168 h. Fractional strain energy was obtained from the aged modulus and tensile strengths of the samples at intervals of 48, 96, and 168 h, using the following formula:

$$f(x) = \frac{\text{(Aged tensile} \times \text{Aged elongation)}}{\text{Initial tensile} \times \text{Initial elongation}} \times 100$$

### Hardness

The hardness test was carried out in an IRHD hardness tester as per ASTM D1415.

### Abrasion loss

Abrasion loss (mm<sup>3</sup>) was obtained from a Zwick Abrader as per DIN 53516.

### Heat buildup

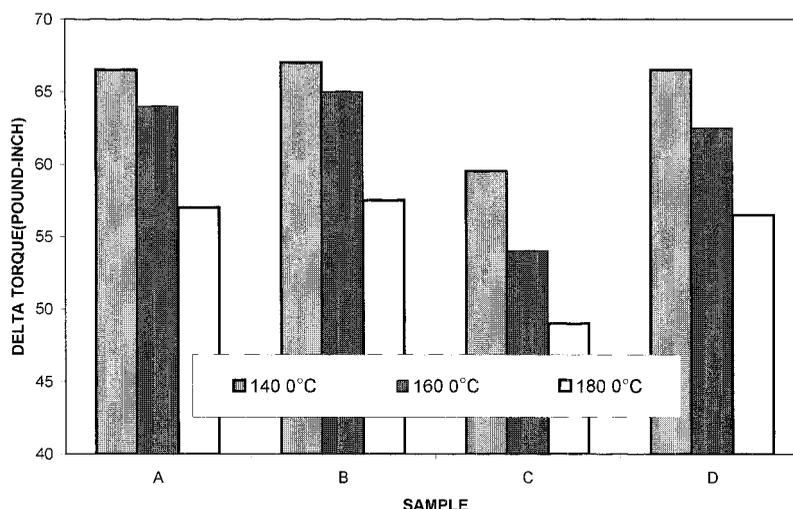
The heat buildup was obtained from a Goodyear Flexometer using ASTM D623.

### Hysteresis loss

The hysteresis loss (%) was obtained in a Instron 6021 Universal Testing Machine.

### Scanning electron micrograph

A scanning electron micrograph (SEM) was taken of the gold-coated fracture surfaces of the tensile strips



**Figure 1** Variation of delta T (rheometric torque) at three different temperatures for the different compounds.

and the gold-coated abraded surfaces of the abraded specimens. The SEM was taken in a Hitachi SEM S354 model using an electron beam potential of 25 kV at magnifications of 300, 500, and 750.

### Dynamic mechanical properties

Dynamic mechanical properties were measured by a Dynamic Mechanical Thermal Analyser, Mark II, DMTA (Polymer Laboratories Limited) to obtain the  $\tan\delta$  values at temperatures of 25 and 60°C at a frequency of 10 Hz. Deformation was applied in the cantilever flexure double-clamping mode.

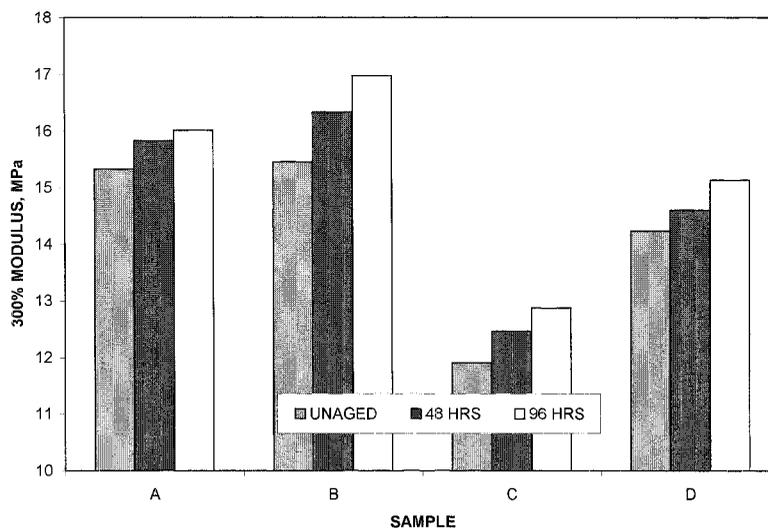
## RESULTS AND DISCUSSION

From the results obtained, can be observed that there has been a marked change in the properties of the test

samples. This is evidently due to the interaction of trihydroxy benzene with the carbon black. The authors, in their earlier investigation with metahydroxy benzene,<sup>7</sup> established by Fourier transform infrared (FTIR) studies that the concerned functional group, phenolic —OH, was responsible for the surface modification, thus altering various thermomechanical properties.

In the present investigation, it was found that Compound B initially showed improved rheological properties. However, further investigation revealed that these were becoming overshadowed by the improved physicommechanical and dynamic properties of Compound C. The following discussion explains the phenomenon.

The rheometric modulus obtained for various samples has been plotted for different temperatures (Fig. 1). The delta torque of rheological cure curves has



**Figure 2** Variation of unaged and aged 300% modulus for the different compounds.

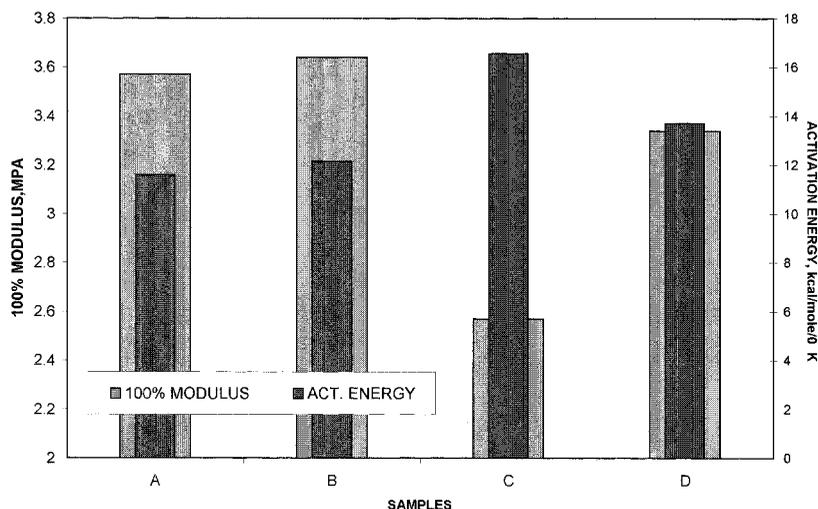


Figure 3 Variation of unaged 100% modulus and activation energy for the different compounds.

been found to be higher for Compounds A and B, but lower in the case of Compound C. Similar behavior has also been obtained for the static modulus at 300% elongation (Fig. 2), with Compound B showing appreciably higher modulus as against the normal compound. Oxidative aging at 70°C for 48 and 96 h, though, shows a decrease in the magnitude; the trend of each of the compounds, however, remains the same (Fig. 2). The phenomenon of higher modulus may be due to stress-induced crystallization of natural rubber and also may be due to formation of higher crosslink density. The inference of high crosslink density may further be supported by the fact that these compounds have a higher modulus at 100% elongation (Fig. 3). The magnitude of crosslink density is proportional to the modulus at 100% elongation as is evident from the following equation<sup>9</sup>:

$$(2M_c)^{-1} = E/3\rho RT$$

where  $(2M_c)^{-1}$  is the crosslink density,  $E$  is the modulus at 100% elongation (MPa),  $\rho$  is the density of rubber ( $\text{kg/m}^3$ ),  $R$  is the universal gas constant ( $\text{J/mole K}$ ), and  $T$  is the absolute temperature (K).

The compounds have lost all their strength after a period of 168 h of aging, which may be due to the pronounced capillary effect of the low thickness slab. Fractional strain energy (Fig. 4) has been highest in the case of Compound B, possibly due to the maximum retention of bonds and its rearrangement in the elastomer matrix during induced stress.

The apparent activation energy calculated from the Arrhenius equation showed that minimum energy is required for vulcanization for Compound B (Fig. 3). This is apparently due to the formation of a bridge with the remaining active sites after competing with the vulcanization reaction.

Interestingly, the results of abrasion (Fig. 5), heat buildup, hysteresis loss (Fig. 6), and the  $\tan\delta$  values at

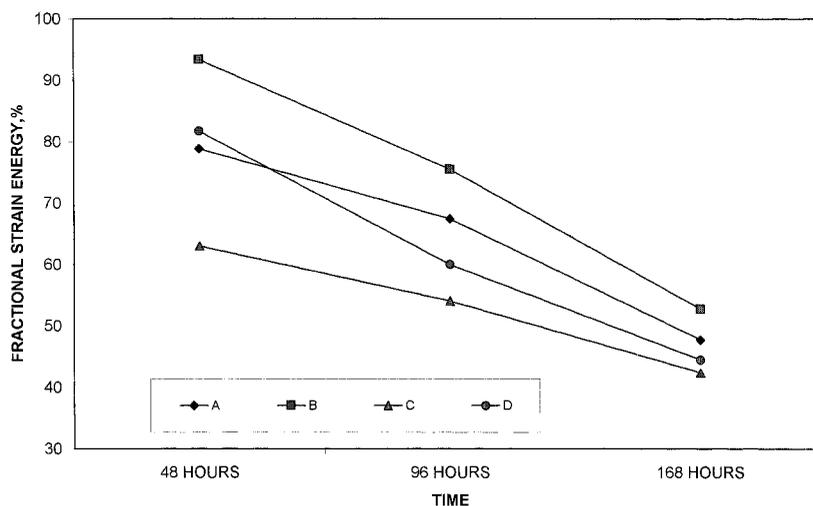
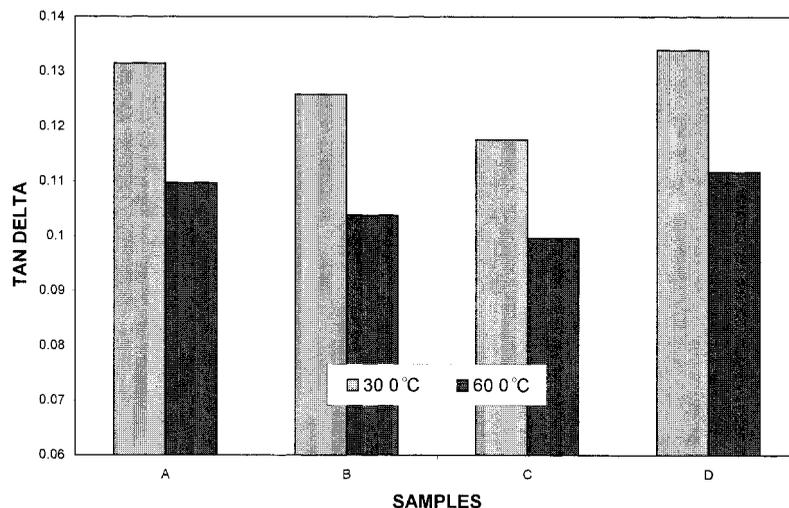


Figure 4 Fractional strain energy variation at three different intervals of aging for the different compounds.



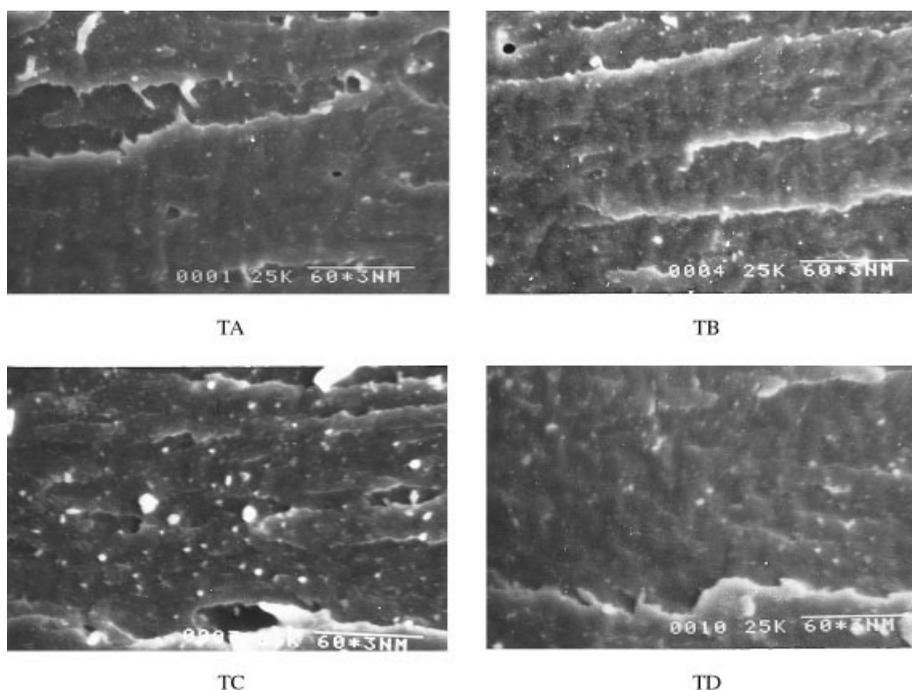


**Figure 7** Variation of  $\tan\delta$  values obtained at a temperature of 25 and 60°C at a frequency of 10 Hz for the different compounds.

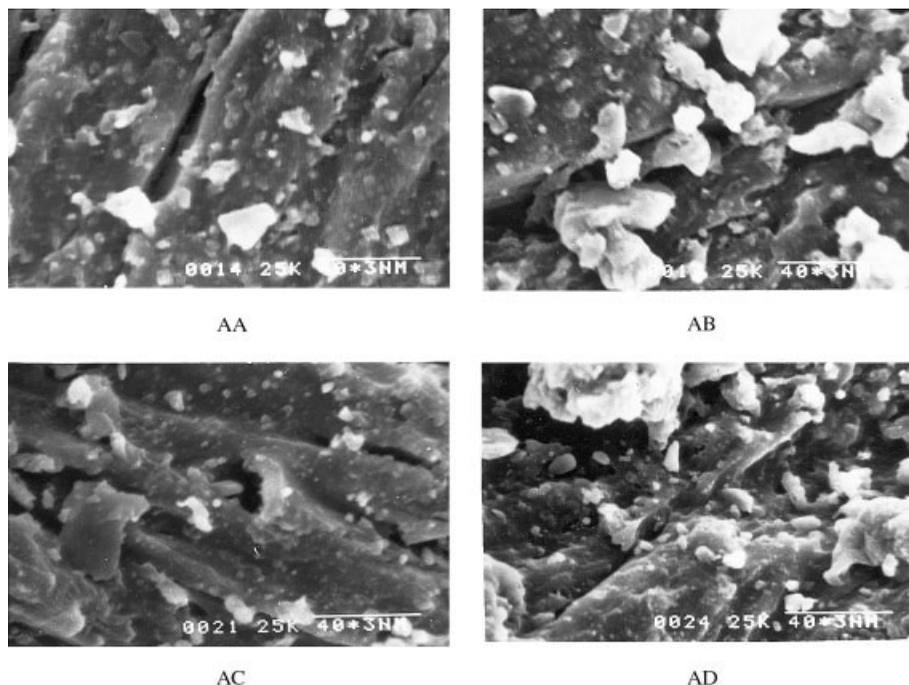
benzene<sup>7</sup> confirm the above phenomenon. These linkages generally increase with the increase in hydrodynamic effect, contributing to better polymer–filler interaction by bridge bonding. As a result, the present system shows better Mullin’s Effect<sup>11,12</sup> and Payne’s Effect.<sup>13,14</sup>

The SEM micrographs further support the above phenomenon. The micrograph of the torn tensile sample pieces shows a slightly nonhomogeneous but clean nature in case of the abraded surface. This is generally due to partial solid–solid mixing. Shear displacement is no-

ticed on few widely separated slip planes. A separation of slip planes showed maximum reduction with compound C due to the best polymer–filler interaction. These slips are taking place along with the slip plane’s direction when the corresponding component of shear stress reaches the critical value for this compound. The effect of twining on the fractured surface was also observed to be the least in the case of compound C. This phenomenon was observed at the edge dislocation structure. Compound C also shows the phenomenon of large shear displacement with sharp boundaries of disloca-



**Figure 8** TA, TB, TC, and TD: SEM micrographs of tensile fracture samples of A, B, C, and D, respectively, at 500× magnification.



**Figure 9** AA, AB, AC, and AD: SEM micrographs of abraded samples of A, B, C, and D, respectively, at 750 $\times$  magnification.

tion, compared to other compounds, especially for the abraded samples, due to knotty tear for better reinforcement. (See Figs. 8 and 9.)

The above observations thus evidently explain and corroborate the improved results of abrasion loss, heat buildup, hysteresis loss, and the  $\tan\delta$  values of the modified Sample C.

The slight decline in the modulus values for Compound B is probably due to the formation of pseudo-linkages resulting in the higher cage effect above the optimum hydrogen bonding coupled with the effect of the breakage of the weak interparticle bond as explained by Payne and Whittaker.<sup>15</sup>

### CONCLUSION

From the above results it may be concluded that the aqueous solution of 1,3,5-trihydroxy benzene has an appreciable effect on the physical and the dynamic mechanical properties of the natural rubber compound with surface-modified carbon black. It can be seen that the moduli, both rheometric and static, are better for the compound with the medium dosage of the additive. The lower values of abrasion loss, heat buildup, and hysteresis loss are obtained for Compound C. The  $\tan\delta$  values obtained at temperatures of 25 and 60 $^{\circ}$ C at a frequency of 10 Hz are also found to be better for Compound C. SEM micrographs corroborate the above facts. These properties combined would provide an excellent service condition for Compound C for a truck tire tread with low rolling resistance.

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