

Effect of *meta*-Dihydroxy Benzene as a Surface Modifier on Filler–Filler and Filler–Polymer Interaction of Carbon Black Polymer Composite

S. GANGULY,¹ S. CHAKRABORTY,¹ A. N. BANERJEE,² P. BHATTACHARYA³

¹ Phillips Carbon Black Limited, Durgapur 713 201, India

² Department of Polymer Science and Technology, University of Calcutta, Calcutta 700 009, India

³ Department of Chemical Engineering, Jadavpur University, Calcutta 700 032, India

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ABSTRACT: In the present context an attempt was made to use polyhydroxybenzene on rubber-grade carbon black to suitably modify the surface morphology and hence to achieve improved thermomechanical and mechanical dynamic properties. FTIR studies clearly point out the presence of excess hydroxyl group in the modified black. The improvement in mechanical properties is attributed to higher crosslink density through hydrogen bonding and oxygen bridge participation during the covulcanization reaction. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 2025–2033, 2002

Key words: surface modification; *meta*-dihydroxy benzene; crosslink density; Mullin's effect; van der Waals force

INTRODUCTION

Carbon black, when used as a filler in polymeric substances has a range of physical and chemical attributes (particle size, surface area, structure, surface activity, etc.) and can change elastomer properties in different ways and to different extents. While compounding, it is necessary to select the proper polymer and suitable quality of carbon black having the appropriate level of combination. The vulcanization system should also include a suitable accelerator and the entire system should be cost-effective.

An extensive survey of the literature shows that surface modification by Si-69,¹ aliphatic di-

hydric, and trihydric alcohol,^{2,3} imparts improved hysteresis and improved abrasion-resistance properties at low and high temperatures compared to those of carbon black without any modification. It is also reported that surface modification by a silane coupling agent leads to a decrease in reinforcement.⁴ Carbon black with phenolic plant product⁵ gives flex crack growth resistance and carbon black modified with vegetable oil⁶ shows high tensile strength and elongation properties, and low abrasion and hardness. It was felt that a systematic study in this area was necessary to establish the optimum process parameter for its commercial acceptability; here, we investigated the effect of the hydroxyl group in general and the aromatic hydroxyl group in particular. Resorcinol,⁷ a *meta*-dihydroxy benzene, was selected to study its effect as a chemical for surface-modified black.

Correspondence to: A. Banerjee.

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Table I Sample Identification and Composition

Sample A	Sample B	Sample C	Sample D
500 g Black (N220) and 50 cm ³ 0.005% resorcinol solution in water	500 g Black (N220) and 50 cm ³ 0.1% resorcinol solution in water	500 g Black (N220) and 50 cm ³ 1.0% resorcinol solution in water	500 g Black (N220) without any additive

The objective of this investigation is to explore the possibility of imparting improved properties with respect to both surface chemistry of carbon black and of the associated polymer by changing the concentration of resorcinol, which acts as the surface modifier. It is expected that it will give better reinforcement than normal black, as reflected in the studies.

EXPERIMENTAL

Materials Used

Natural rubber (NR) (RMA-1X) had a moisture content 1%, ash content 0.4%, specific gravity 0.9, and Mooney viscosity (ML 1+4 at 100°C) 60. Zinc oxide (Merck, Darmstadt, Germany) and sulfur (Qualigen) were of laboratory reagent grade. Accelerator *N*-oxydiethylbenzthiazyl sulfenamide (NOBS) and peptizer pentachlorothiophenol (PCTP) were from ICI (India). The carbon black Orient Black N220 was from Phillips Carbon Black Limited, India. The resorcinol (Loba Chemie) was of laboratory grade.

Preparation of Modified Carbon Black Sample

Three different strengths of aqueous resorcinol solution were made and sprayed over the dryer discharge product of the carbon black sample (temperature 170°C) with uniform stirring to ensure proper mixing. Details of the composition of the carbon black and the resorcinol solution along with the respective sample identification are given Table I. It was ensured that the samples were free of moisture before mixing. The untreated carbon black had a di-*n*-butyl phthalate (DBP) absorption value (ASTM D2414) of 113.0 mL/100 gm, crushed DBP absorption value (ASTM D3493) of 99.0 mL/100 gm, iodine number (ASTM D1510) of 120.3 mg/gm, cetyl trimethyl ammonium bromide (CTAB) (ASTM D3765) of 112.0 m²/gm, and tint strength (ASTM D3265) of 113% TRB. 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 × 12in.) at a friction ratio of 1:1.4 and front and back roll speeds of 24 and 33 rpm, respectively, at 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 the same level of polymer–filler interaction. The compounds were identified according to the identification of the carbon blacks that were mixed.

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

Rheometry

After maturation for 24 h, rheometer data were obtained in a Monsanto R-100 model (Monsanto, St. Louis, MO) at ±3° arc and 100 range scale at temperatures of 140, 160, and 180°C.

Mechanical Properties

Dumbbell-shape samples were prepared from cured sheets and these were 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. The thickness of the samples was measured by a bench thickness gauge.

Hardness

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

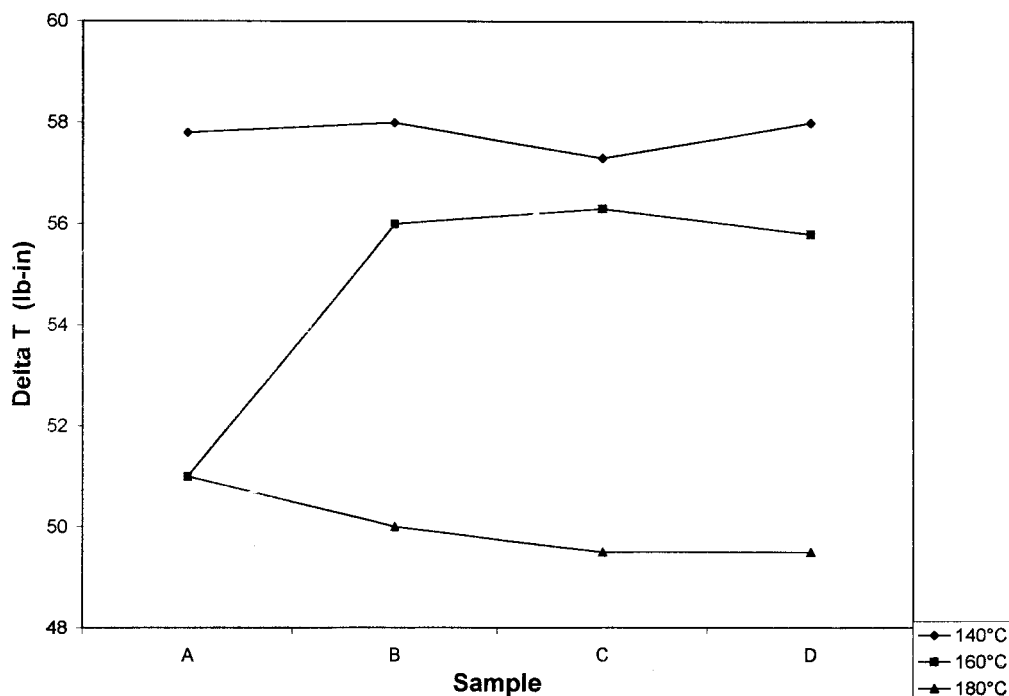


Figure 1 Variation of ΔT (rheometric torque) at three different temperatures for the different compounds.

Abrasion Loss

Abrasion loss (mm^3) was obtained from a Zwick abrader according to DIN 53516.

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 192 h and results were obtained at three different intervals of 60, 120, and 192 h. The fractional strain energy was obtained using the formula:

$$f(x) = (\text{aged tensile} \times \text{aged elongation} / \text{initial tensile} \times \text{initial elongation}) \times 100 \quad (1)$$

Hysteresis Loss

The hysteresis loss (%) was obtained by an Instron 6021 Universal Testing Machine.

FTIR Analysis

A very thin section of the cured compound was analyzed in a Perkin-Elmer Spectrum RX FTIR

analyzer (Perkin Elmer Cetus Instruments, Norwalk, CT) in ATR mode with germanium prism. A resolution of 4 cm^{-1} was given over 64 scans at a prism angle of 45° .

RESULTS AND DISCUSSION

The apparent crosslinking density (i.e., rheometric modulus) was plotted against *meta*-hydroxy benzene content in N220 carbon black for use in the rubber compound (Fig. 1 and Table II). The maximum extent of cure is equivalent to the difference of maximum torque and the minimum torque. This was found to be highest for compounds B and D at 140°C , for compounds B and C at 160°C , and for compounds A and B at 180°C (Fig. 1).

Further, the crosslinking density is directly proportional to the modulus at 100% elongation, which can be obtained from the following equation⁸:

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

where $(2M_c)^{-1}$ is the crosslink density; E is the modulus at 100% elongation, MPa; ρ is the den-

Table II Rheometric Results of the Four Compounds at Three Different Temperatures

	140°C		160°C		180°C	
	$t_{90} - t_{s_2}$ (min)	Cure Rate (lb.-in./min)	$t_{90} - t_{s_2}$ (min)	Cure Rate (lb.-in./min)	$t_{90} - t_{s_2}$ (min)	Cure Rate (lb.-in./min)
A	33.0	1.576	7.25	7.03	3.25	15.69
B	28.5	1.83	8.375	6.69	3.375	14.81
C	30.2	1.97	8.375	6.72	2.875	17.22
D	26.5	1.97	5.625	9.92	3.0	16.5

sity of rubber, kg/m^3 ; R is the universal gas constant, J/mol K ; and T is the absolute temperature, K .

The crosslink density is highest for compound B because of higher modulus at 100% elongation (Fig. 2). The apparent activation energy was calculated from the Arrhenius equation. It is observed that minimum energy is required for vulcanization for compound B (Fig. 2). This is probably attributable to the formation of a bridge in the remaining active sites left after competing with the vulcanization process.

No appreciable change was observed in the unaged physical modulus. Its magnitude was slightly higher for compound B than for the normal compound. Similar trends were observed for the aged compound for 60 and 120 h at 70°C . The aged compound at 192 h lost all its strength as a result of overaging (Fig. 3), which is ascribed to stress-induced crystallization of the NR compound and that 192 h of aging is very severe for pronounced capillary effect on the low thickness test slab.

Fractional strain energy retention is maximum in the case of compound B (Fig. 4) because of

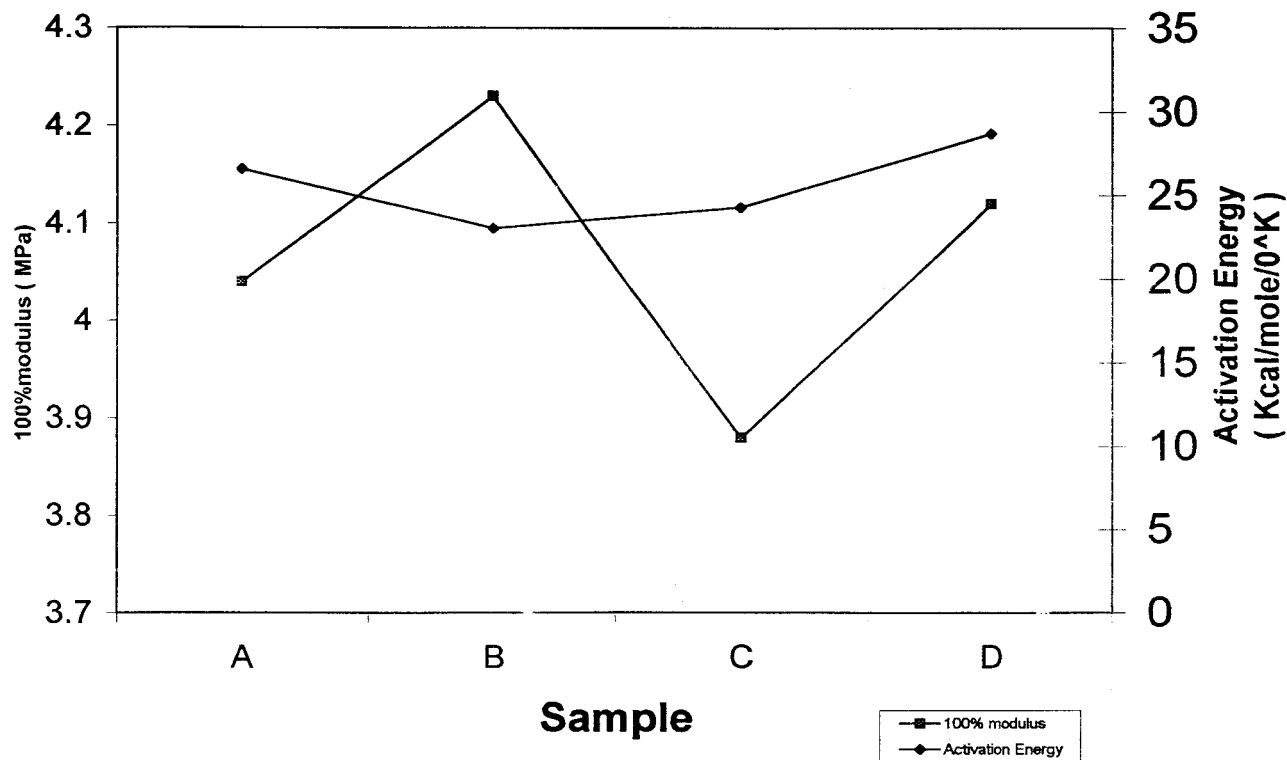


Figure 2 Variation of unaged 100% modulus and activation energy for the different compounds.

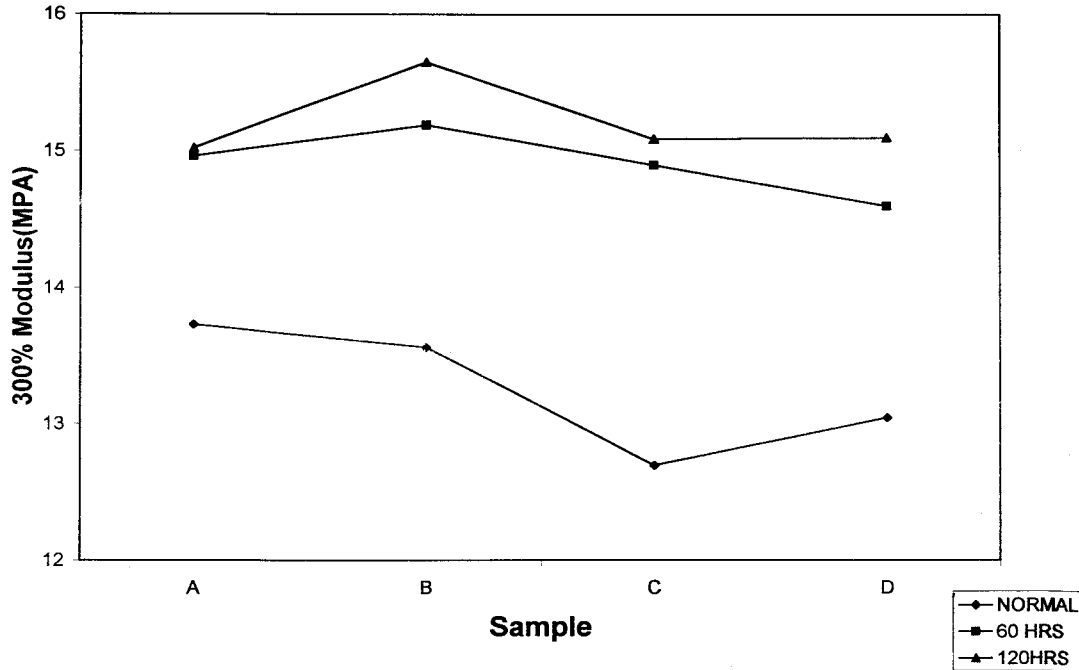


Figure 3 Variation of unaged and aged 300% modulus for the different compounds.

maximum occupation and rearrangement of bonds in elastomer matrix for this compound.

The hardness decreased sharply for compounds C and D, where minimum amount of resorcinol and no resorcinol were employed, respectively. The abrasion loss showed an opposite trend, where loss is minimum in compound B followed

by a sharp increase in compounds A, C, and D (Fig. 5). This evidently indicates that crosslinking occurred through higher reinforcement as a result of oxygen binding.

The Mullin’s effect, that is, stress softening, is greatly pronounced in other compounds compared to that in compound B, in which case it is mini-

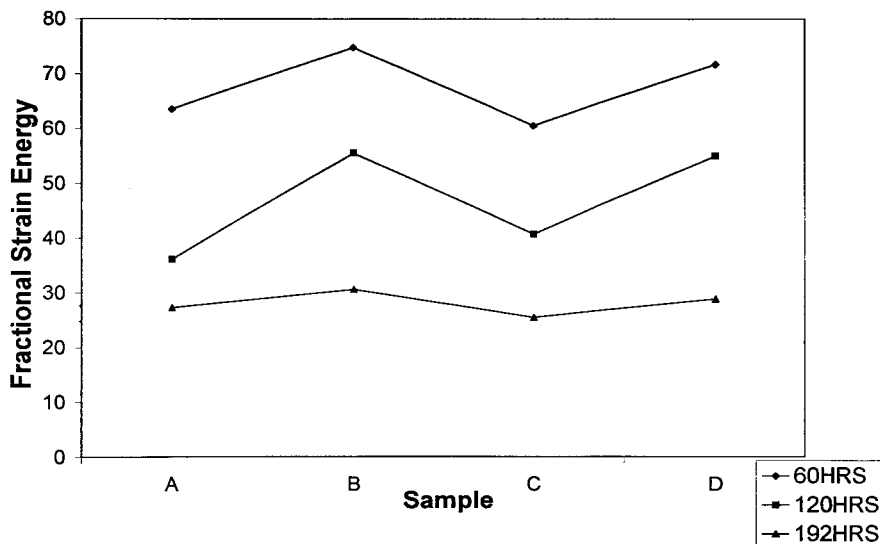


Figure 4 Fractional strain energy variation at three different intervals of aging for the different compounds.

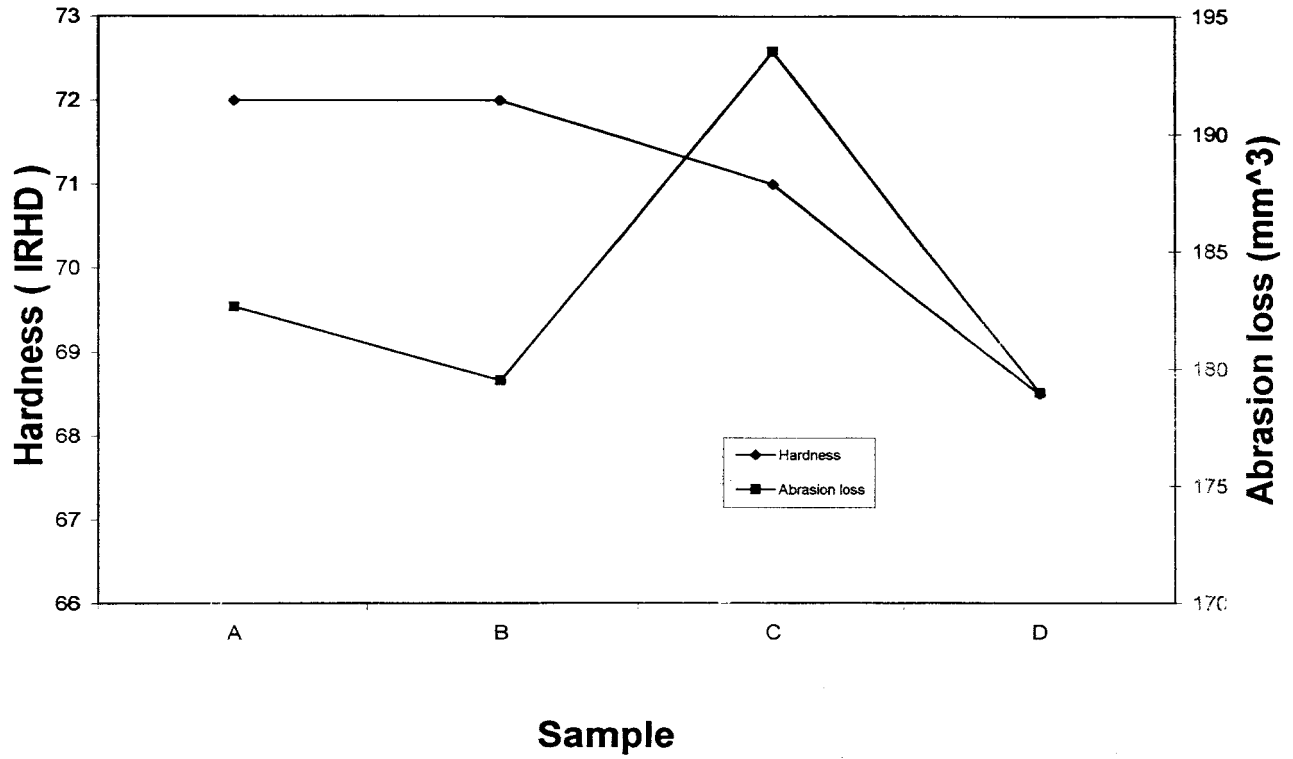


Figure 5 Variation of abrasion loss and hardness for the different compounds.

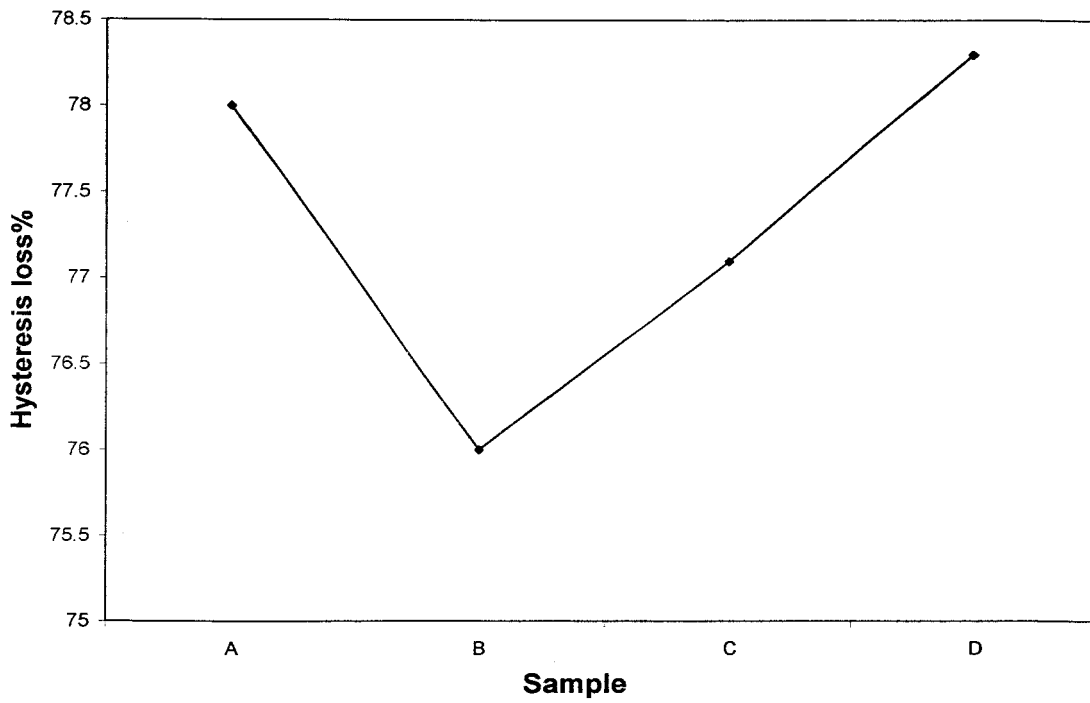


Figure 6 Variation of hysteresis loss for the different compounds.

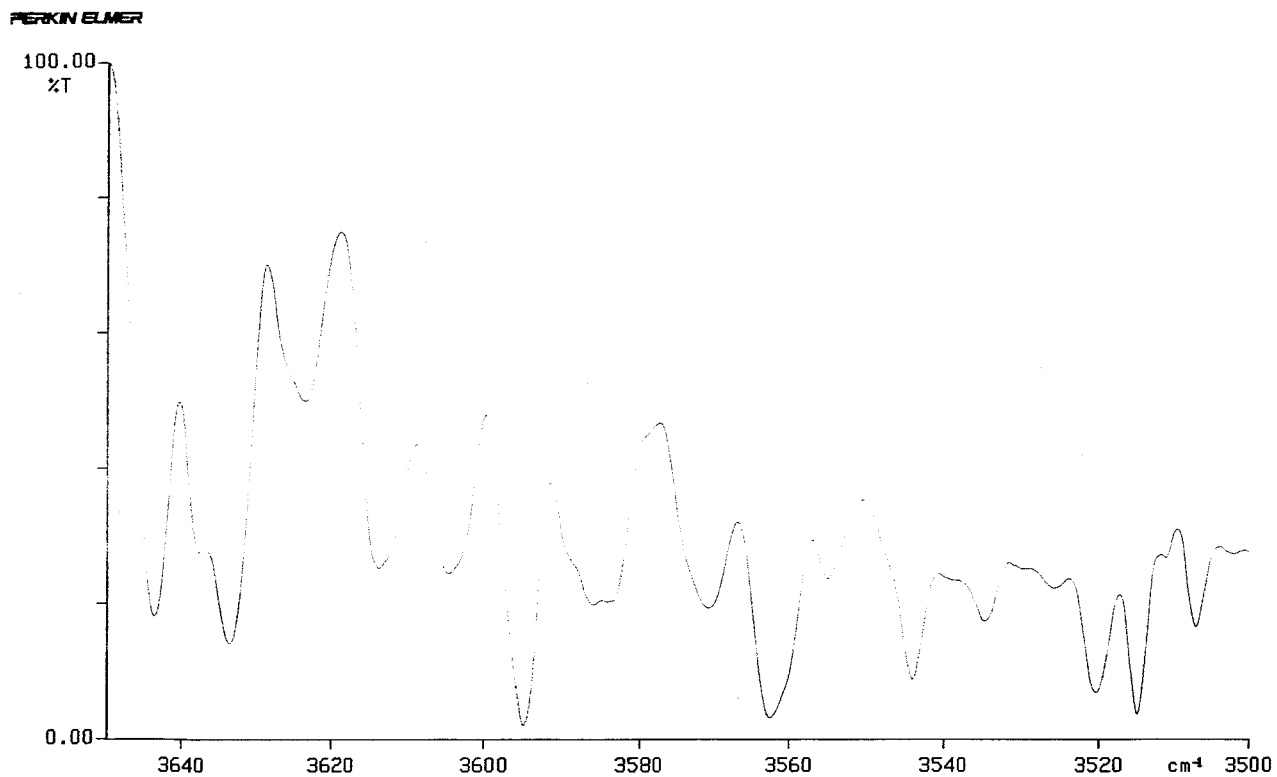


Figure 7 FTIR graph of compound A.

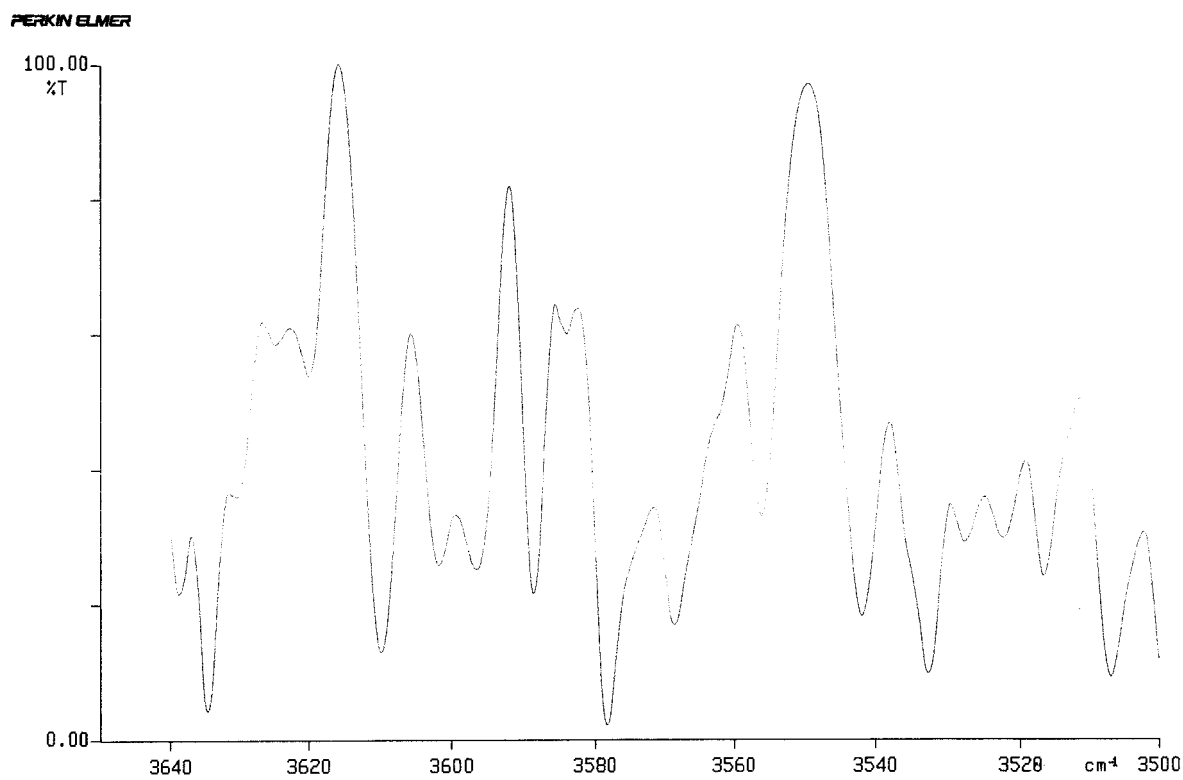


Figure 8 FTIR graph of compound B.

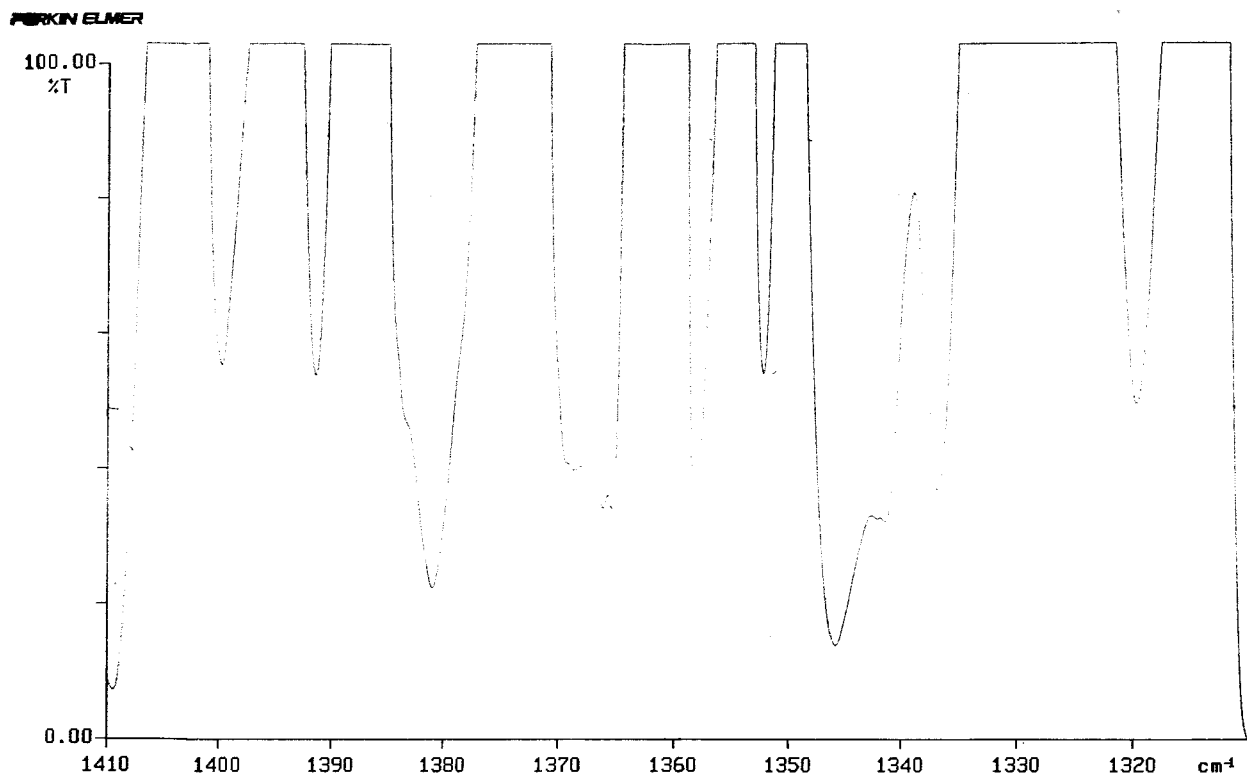


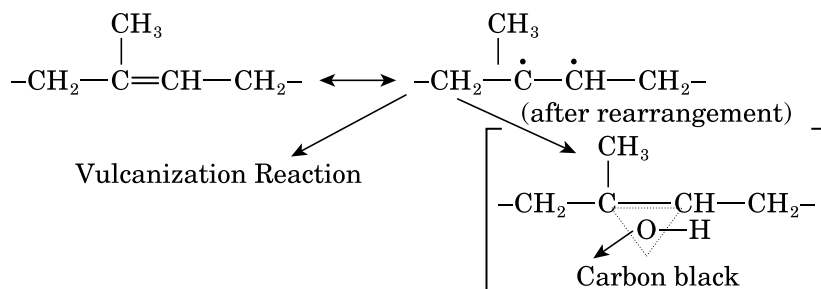
Figure 9 FTIR graph of compound C.

mum (Fig. 6), as indicated from static hysteresis curve. This is possibly attributable to better utilization of available active sites.

FTIR studies show the presence of a prominent hydroxyl group bound in the surface of the filler-elastomer matrix vulcanizate. This was evident from the dual and deep peak obtained from compounds A and B, and the other two compounds where *meta*-hydroxy benzene concentration is minimum or nil (Fig. 7-10).

From the above results it is evident that *meta*-dihydroxy benzene has certainly changed the surface chemistry of normal carbon black, which is taking part in the vulcanization reaction of rubber composite through new sites of crosslinking over and above the normal cage effect of filler-rubber composite through van der Waals forces.

A proposed hypothesis and a possible mechanism are given below:



It has been seen from Table I that sample B with 0.1% resorcinol shows the best and most balanced result in all respects, probably because

of the optimum level of hydroxyl ion concentration participating in the respective site of the elastomer during the vulcanization process. On

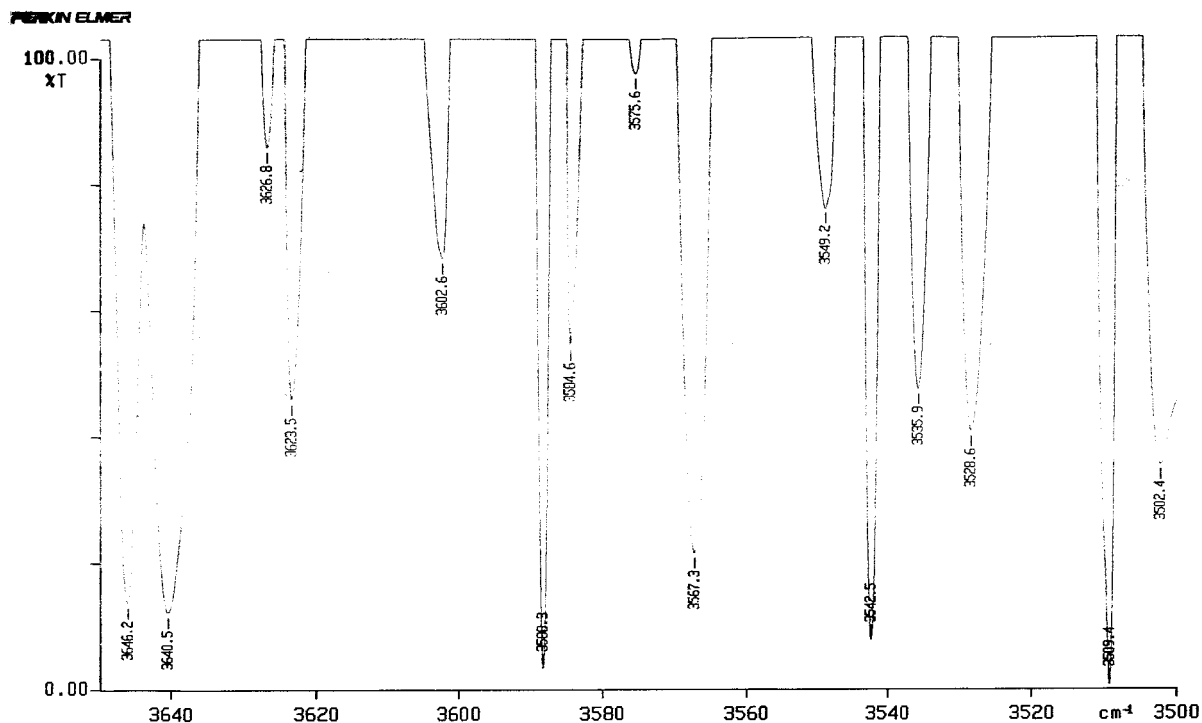


Figure 10 FTIR graph of compound D.

the other hand, the inadequate hydroxyl ion concentration for sample A and excessive concentration of hydroxyl ion for concentration C are responsible for the unsatisfactory concentration.

CONCLUSIONS

From the above results it may be concluded that *meta*-dihydroxy benzene, when used as a surface modifier for carbon black, improves the thermo-mechanical and mechanical dynamic properties. The optimum concentration of *meta*-dihydroxy benzene solution gives the best average results. The rheometric modulus (i.e., apparent crosslink) seems to be improved at this concentration. It also gives a better crosslink density, resulting in high unaged physical modulus, better hardness, and less abrasion loss. The stress-softening effect was more pronounced on other concentrations than in this concentration. The improved properties may be possible because of a new site of crosslinking through van der Waals forces.

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REFERENCES

1. Cabot Corp., PCT Int. Appl. 96 37 547, 1996; U.S. Pat. 528,895, 1995.
2. Nippon Steel and Chemical Co., Jpn. Kokai Tokkyo Koho 10 25, 429 [98 25 429], 1998; Jpn. Appl. 96/180, 924, 1996.
3. Nippon Steel and Chemical Co., Jpn. Kokai Tokkyo Koho 10 17, 712 [98 17 712], 1998; Jpn. Appl. 96/176, 814, 1996.
4. Wang, W. D.; Vidal, A.; Nanse, G.; Donnet, J. B. *Kautsch Gummi Kunstst* 1994, 49, 493.
5. Adhikari, B.; *et al.* *Kautsch Gummi Kunstst* 1998, 51, 500.
6. Kundu, P. P. *J Appl Polym Sci* 2000, 75, 735.
7. Chakraborty, S.; Bandopadhyay, D.; Sen, A. *Rubber Chem Rev* 1983, 123.
8. Bhowmick, A. K.; Hall, M. M.; Benarey, H. A. *Rubber Products Manufacturing Technology*; Marcel Dekker: New York, 1994; p 320.